CHEMICAL AND PHYSICAL CHANGES IN A WOOD ASH-AMENDED FOREST SOIL

By

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Land application of wood ash is gaining popularity as an alternative disposal method due to increasing landfilling costs. However, ash application increases soil pH and salinity and affects plant water and nutrient dynamics. This study determined the effects of high-volume wood ash application on (1) trace metal accumulation in soil and groundwater, (2) uptake of plant (slash pine) nutrients and trace metals, (3) the impact of changes in pH and electrical conductivity on the leachability of trace metals and (4) changes in physical properties in a forest soil. Ash application slightly increased soil metal concentrations, but groundwater metal concentrations increased substantially. Soil arsenic concentrations exceeded the United States Environmental Protection Agency (USEPA) Region 4 clean up goals and the groundwater concentrations of Se, Cr and Cd exceeded the National Primary Drinking Water Standard (NPDWS) for a few months before decreasing. The high pH (~8.5) induced by ash application solubilized organic

matter and increased metal leaching into groundwater. Acidification of the ash to pH 6-7 before application reduced the concentration of dissolved organic carbon (DOC) thereby decreasing metal leaching. Although the high pH mobilized large concentrations of DOC at our site, laboratory column studies using ash only showed that most of the fulvic acid fraction of DOC was retained in the matrix due to the high ionic strength. Fulvic acid metal reduced the leachability of some metals (e.g. Cu), but had very little effect on those elements that do not normally complex with organic matter. Total and plant available Ca, Mg, K, Cu, Mn, Fe and Zn increased substantially in the soil after addition of ash. Although plant uptake of trace metals was not enough to cause toxicities in slash pine (*Pinus Elliottii*, *L*), plant biomass was significantly reduced due to nutrient uptake problems caused by the salinity and high pH. Ash application at this site also increased soil water holding capacity and reduced hydraulic conductivity due to its fine texture, but the added salinity may have neutralized this potential benefit by increasing the plant energy requirement for water uptake. Wood ash application should be done conservatively, based on the liming and nutrient requirements of the soil, in order for it to be sustainable.

CHAPTER 1
INTRODUCTION

About 4.6 million metric tons of ash are produced every year from the combustion of wood and coal for energy by the US forest products industry (Vance, 1996). The pulp and paper sector produces about 3.4 million tons to which coal and wood ash contribute 1.7 million tons each. The wood products sector alone produces about 1.2 million tons of ash (Miner and Unwin, 1992; Someshwar, 1996).

Wood ash is produced when wood fines (mostly planar shavings) and chip rejects (from screening operations) are burned as fuel to produce energy in boilers. It includes both fly and bottom ash and other materials that collect in the residue. The production of boiler ash from paper mills and plywood plants in the US continues to grow as demand for paper and plywood products increases. At the same time, the cost of ash disposal has increased drastically.

Landfills, the most popular means of disposal, are also becoming more difficult to site due to high costs, more stringent regulations, diminishing land availability and public opposition (Thacker, 1986). Alternative ways, hence, have to be found to dispose the ever-increasing waste. As a result, land application of ash has now become common as companies use their own land for ash recycling while keeping it in production (Muse and Mitchell, 1995; Naylor and Schmidt, 1989; Ohno and Erich, 1990). In addition, forest

application of ash is not subject to the same stringent regulations as landfill disposal. Consequently, the costs associated with this means of disposal are relatively low.

Many factors need to be considered before boiler ash is applied to land. The chemical and physical properties of the ash and soil at the application site, the long term effects of the application upon the flora and fauna, the cost and regulations that govern the application of non-hazardous and/or non fertilizer materials to land. The costs, state and federal regulations governing land application of wastes, and the chemical and physical properties of ash and soil can be easily determined or accommodated within a short period of time. The long term effects of papermill ash on a particular site, however, need more rigorous research in order to understand the processes that govern nutrient or metal solubility and/or adsorption in the given medium, metal-soil and ash-soil-metal interactions, and leaching properties of ash constituents from ash and soil. These dynamics also rely on the external factors such as land management and climate. This underscores the necessity to study the above factors under both field and greenhouse/laboratory conditions so that land application of papermill ash is carried out in a safe and sustainable manner.

The objectives of this study were to investigate the impact of high-volume boiler ash application on forest soil nutrient status, moisture retention and trace metal loading as well as metal leaching to groundwater. The extremely large application rates used in this study separate it from most of the research that has been done involving wood ashes from various parts of the country. The desire to dispose of the highest possible amount of ash on the least possible area was the main reason for these high application rates. Furthermore, when the ash was applied at our site, little attention was paid to the potential

impact of the chemical constituents of the ash. The focus was on trying to increase moisture retention in the sandy soil in the area.

The study was carried out in two parts. The first part consisted of a field monitoring study in which 15 ¼-hectare plots were monitored for pH, nutrient status, trace metal loading, and groundwater pollution through a period of two years after application of up to 1800 Mg ha^{-1} of ash. The specific contribution of colloids to trace metal transport in the field was also investigated using samples collected in monitoring wells. The second part of the study involved laboratory and greenhouse studies to determine the specific interactions of boiler ash with soil and plants under well-controlled conditions. Specific studies on the potential nutritional benefits and/or toxicity of high volume ash application on slash pine, *Pinus Elliottii,L,* were carried out in a greenhouse study. Laboratory and column studies were conducted to study the effects of organic (humic and fulvic) acids on trace metal leaching under water unsaturated conditions using low flow velocity, and the general effect of acidification of ash on trace metal leaching in saturated columns was studied under pressure. Batch studies were also conducted to determine the desorption curves of metals from ash (from the dissolution kinetics of trace metals from ash) and develop adsorption curves for our soil using pure metal salts. Soil moisture characteristic curves were developed for the different treatments and the changes in other physical properties were determined.

Results from these studies were then synthesized to determine the most important factors that need consideration when boiler ash is land applied. Results from the field soil and groundwater monitoring studies are presented first, followed by various laboratory studies that investigated the mechanisms of the processes affecting trace metal movement

in ash-amended soils in the field. The greenhouse experiment is the last study presented. The last chapter presents a synthesis of ideas from each of these experiments and presents simplified considerations to be accommodated when ash is applied to land.

CHAPTER 2
LITERATURE REVIEW

Wood Ash Production and Properties

Wood ash is the organic and inorganic residue produced from burning of wood chips and other wood residues that are left over when tree bark is trimmed in plywood plants as a first step in plywood processing (Campbell, 1990). This ash is also often mixed with fly ash from the stacks in boilers. Wood residue consumption in the USA amounted to 124 million Mg (oven dry weight), equivalent to about 2487 trillion kJ of energy in 1990 (Energy Information Administration, EID, 1991). This accounted for nearly 3% of all primary energy used in the country that year. Some plywood plants and papermills also use whole trees harvested solely for fuel wood and rejects from lumber manufacturing processes in so called "bark-boilers".

The average ash content in wet bark from 56 pulp and paper mills was about 4% with a median of 2.6% at 50% moisture (Miner and Unwin, 1992). Temperate climate woods were shown to yield less ash (0.1 – 1%) than tropical and subtropical woods which yield up to 5% ash. In general, hardwoods yield more ash than softwoods (Campbell, 1990).

Although wood fired-boiler ash was used in this study, the term "papermill ash" is generally used in the literature to denote various ashes produced at paper mills. In this dissertation, the term wood fired-boiler ash (i.e. boiler ash) is used to refer specifically to

the ash used in this study. The term "wood ash" is used as a general term for the various ashes from different sources.

The properties of wood ash depend on the type of wood utilized, the maximum temperature reached and combustion system used (Campbell, 1990; Catricala et al., 1996). Generally, wood ash consists of salts, oxides and hydroxides of Ca, Mg, Na, and K (Hakkila, 1986; Lerner and Utzinger, 1986) and low amounts of the trace metals including As, Cd, Cr, Cu, Mn, Ni, Se and Zn (Etiegni et al., 1991; McGinnis, 1995; Pepin and Coleman, 1984; Unger and Fernandes, 1990; Williams et al., 1995), with an average pH of 12.4 (Someshwar, 1996). Other elements present include N, S, Al, Fe, Si, Ba and Mo. Nitrogen and S (and sometimes P) are typically low in wood ash as these elements are volatilized from plant biomass upon combustion. Iron and Al can be present in relatively high concentrations depending on how the material is handled before and after combustion. The predominant anions in ash include: chloride, nitrate, and bromide.

The combustion process is also responsible for concentrating the elements in ash due to loss of biomass (mainly compounds of C, S, N and water are lost during combustion). Although ash is low in toxic trace metals, most of these are readily soluble because the solid matrix is mainly composed of salts (Muse and Mitchell, 1995; Unger and Fernandes, 1990).

Wood ash is fine in texture, consisting primarily of particles ranging in size from clay to silt components of soil. The fineness of the particles within the ash also determines its reactivity (Naylor and Schmidt, 1986; Rowell, 1988) with powdered forms being more reactive than granulated forms (Clarholm, 1994). Powdered forms also generally react faster with soil chemical components than commercial fertilizers and this

often leads to their effects on soil chemical and physical properties being short lived compared to conventional fertilizers.

The chemical and physical properties of various wood ashes produced throughout the United States are shown in Table 2-1. Care should be taken when comparing these mean values because moisture and carbon content and ash type vary considerably between different industrial ashes. The wide ranges associated with some of the chemical and physical parameters are testimony of this. For example, Mn, P, and B concentrations

Table 2-1. pH, calcium carbonate equivalent, micronutrient and macronutrient concentrations of boiler ashes from different sources.†

Variable	Median	Range	No of samples
PH	12.3	7.80 – 13.1	23
CCE‡	48.1	13.2 – 92.4	18
Macronutrients		---- g kg^{-1}---	
P	4.20	0.30 – 14.4	24
K	27.9	1.90– 130	25
Ca	180	35.9 – 966	25
Mg	9.70	3.20 – 24.7	25
N	0.60	0.20 – 0.90	8
Micronutrients		--- mg kg^{-1}--	
Mn	2430	0.33 – 7820	25
Cu	70.4	37.7 – 207	25
Zn	316	35.2 – 1250	25
B	91	7.70 – 290	6
Mo	12.6	3.00 – 123	16

†From Naylor and Schmidt (1986), Campbell (1990), Etiegni et al. (1991) and Muse (1993)
‡ percent calcium carbonate equivalent

vary across three orders of magnitude among the ashes. It must also be noted that these data do not necessarily represent the whole cross-section of all the different types of ash produced in this country. They only represent data that were available to the author.

Because wood ash has a very rich chemical and mineral composition, its addition to soil can potentially change physical properties of sandy soils and improve soil fertility if it is applied at agronomic levels. In addition, wood ash generally has an alkaline pH and is high in salts. Thus high volume application of ash may have an adverse impact on soil by elevating soil pH and increasing soil salinity (both of which have deleterious effects on plant growth). The high pH comes from additives like sodium hydroxide, used for priming by some plywood plants, and the aqueous hydroxides of some of the cations from group I and II of the periodic table found in the ash (Na, K, Ca and Mg).

The ash used in this study was from a plywood plant, owned by Georgia Pacific Corporation, located in Hawthorne, Florida which produces approximately 4 Mg of ash a day. The company owns several other plants in the Southeast and each of them produces several tons of ash a day. Selected chemical and physical properties of this ash are shown in Table 2-2. The characteristics shown in this table are for the batch that was used in this study. If the temperature of combustion, the type of wood used and additives change, the composition of ash from different batches from the same boiler may vary significantly. The composition of the ash is also dependent on the conditions and duration of storage. If the ash is stored outside without cover protection or lining material, its constituents are subject to leaching. It can also adsorb carbon dioxide from the atmosphere forming carbonates (e.g. calcite) within the matrix. Table 2-3 shows some common reactions of wood ash components during and after combustion.

Table 2-2. Elemental concentrations and related chemical properties of the ash and soil used in this study

Element	Boiler ash (fresh)		Soil (A horizon)		Boiler ash/soil concentration ratio
	Total	Available	Total	Available	Total
	---------- mg kg^{-1} ----------				
Ca	100,000	463	130	58.6	190
Mg	9,000	363	900	4.40	10
K	8,000	1760	30	5.80	267
P	3,000	14.0	100	0.00	30
Fe	7,000	71.6	800	13.1	9
Mn	860	26.5	14.0	3.50	60
Zn	329	27.7	0.7	0.07	470
Cu	37.0	5.63	1.0	0.10	37
	Total		Total		
Al	8000		2000		4
Na	26000		40		650
Ba	177		7.00		26
Pb	60.0		1.30		46
Se	19.0		0.70		27
Ni	10.0		5.00		2
Cr	2.00		4.00		0.5
As	2.00		0.40		5
Cd	3.00		0.50		6
$CaCO_3$	250000		0.00		-
PH	11.4		5.6		
EC (dsm-1)	78.0†		2.00		
CEC (cmol kg^{-1})	-		4.00		
CCE‡ %	20		-		
OM %	25.0		<1.00		
Sand %	48.1		94.9		
Silt %	34.0		1.9		
Clay %	31.2		3.2		

† This value represents the EC immediately after incorporating ash into the soil. The EC decreased to ~ 10dS m^{-1} after one and half years of leaching.

‡ Calcium carbonate equivalence

The sand, silt and clay fractions in the ash were determined using the pipet method. The limitations of this determination were that most of the components of the ash are soluble in water and this underestimated the percentage of the clay fraction.

Table 2-3. Common reactions of some wood ash components[‡]

Reactants	Products
$Wood + O_2$	$Charcoal + CaO + K_2O + M_xO_y + CO_2 + H_2O$
$CaO + H_2O$	$Ca(OH)_2$
$Ca(OH)_2 + CO_2$	$CaCO_3 + H_2O$
$CaCO_3 + H_2O + CO_2$	$Ca(HCO_3)_2$
$K_2O + H_2O$	$2KOH$
$2KOH + H_2O$	$K_2CO_3 + H_2O$

Source : Campbell (1990)[‡]

Disposal Methods and Current Regulatory Laws

The most popular disposal practices for wood ash include the use of settling ponds (before separating solids for landfilling), stockpiling, and landfilling. On average, over 80% of the ashes from the pulp and paper mills and plywood plants are disposed of in landfills or lagoons, 15% is used as amendment for covering landfills and as a bulking and odor control agent in sludge composting facilities (Maltby, 1989), and 5% is land applied (Campbell, 1990; Gray and Rock, 1987; Miner and Unwin, 1992). Land application is more popular in the Northeastern states where 10% of wood ash is applied to land (Campbell, 1990).

Eighty percent of all landfills being used right now will reach capacity in less than 20 years (Miner and Unwin, 1992). Landfills are, however, becoming more difficult to site due to high costs, more stringent regulations and diminishing land availability (Thacker,

1986). For example, the average tipping fee in Florida is $43 per ton (varying between $23 and $92 per ton depending on location [Florida Department of Environmental Protection - FDEP, 1999]). For companies that produce large amounts of ash like Georgia Pacific, these costs (plus transportation) can add up very quickly. In some states, e.g. Maine and New Hampshire, the tipping fees for secure landfills with liners and leachate collection and control systems varied between $55 and $75 a ton in 1989 (Ginn, 1989) and have substantially increased in the last decade. Viewed in this light, the logic behind the greater emphasis to use land application in these states becomes very apparent.

Public opposition also plays a big role in siting landfills. Nowadays, people are more aware of the dangers posed by leachates that may seep into groundwater sources from landfills. In addition, the NIMBY (not in my back yard) factor has to be dealt with for various other reasons that may have nothing to do directly with pollution. For example, landowners fear, quite justifiably, that property values will go down if they have a landfill in their backyard. County and state officials have to take this into consideration when they make decisions, especially if they hold elected positions.

Forest responses to ash application have been studied most intensively in Scandinavian countries (Eriksson, 1994; Morris and Miller, 1994; Pierce et al., 1993). The relative abundance of forest areas and the increased difficulty in disposal of ash in landfills in these regions forced the affected parties to pursue this alternative disposal channel earlier than others.

In the United States, many state regulating agencies do not have clear-cut regulatory guidelines for wood ashes. In fact, most of the regulations are based on sewage sludge application laws which are being modified to accommodate wood and coal ashes.

Ash classification actually varies from state to state with the generally accepted definition being that wood ash is a non-hazardous waste. Some states like Washington, regulate wood ash as a hazardous waste when its pH is higher than 12.5. This is based on the Federal Resource Conservation and Recovery Act (RCRA) of 1978 (Whitaker and Childs, 1999) which considers materials hazardous (based on their corrosivity) if their pH is below 2 or above 12.5. However, most states do not have pH guidelines for solid wastes (California Air Resources Board, 1990). In Maine, ash is classified as a specified waste, requiring regulatory approval before application to land (Maine Department of Environmental Protection-MDEP, 1989). This is based on modified sewage sludge regulations that consider cumulative total load of heavy metals and threshhold values of trace metals in soils. The state of Oregon allows the application of ash as a beneficial industrial by-product and no permits are required although quarterly and annual reports are needed to identify areas where ash has been applied. In Florida, ash is not classified as a hazardous waste but it can not be applied as a liming amendment because its calcium carbonate equivalence (CCE) is not above 80% (a crucial requirement for all liming materials in the state; [Florida Department of Agriculture and Consumer Services, 1999, personal communication]). It can however be applied as a non-hazardous waste with nutritional benefits because it does supply a significant amount of plant nutrients (K, Ca, some P, and Mg) and micronutrients (Cu, Fe, Mn and Zn).

The permitting process in many states takes an average of six months (Hatch and Pepin, 1985). This generally involves the identification of sites, field investigation of sites, completing required state applications, notifying abutting landowners and local officials, and obtaining the relevant state DEP approval.

Beneficial Aspects of Land Application of Wood Ash

Supply of Plant Nutrients

Campbell (1990), Someshwar (1996) and Vance (1996) provide excellent reviews on the nutritional importance of wood ash. Wood ash application has, for a long time, been recommended as a way of mitigating nutrient imbalances stemming from natural weathering of soil (Cronan and Grigal, 1995; Unger and Fernandez, 1990) and from the effects of acid deposition (Bonneau et al., 1991; Huettl, 1989). In fact, wood ash was specifically produced in the United States for the sole purpose of providing potash for fertilizer from the 18th to the early 20th century (Campbell, 1990). The benefits of ash also form the backbone of shifting cultivation practiced in some parts of East and Central Africa. Even Roman scientists and scholars and early biblical references mentioned the benefits of returning ashes to land (Tisdale et al., 1985).

In more recent times, several researchers have shown that wood ash supplies significant amounts of plant-available Ca, Mg and K to agricultural soils (Campbell, 1990; Erich and Ohno, 1992a; Naylor and Schmidt, 1986, 1989). Naylor and Schmidt (1986) showed that when an industrial ash, equivalent to 0-1-3 NPK fertilizer, was mixed with two soils at application rates ranging from 0 to 36 Mg ha^{-1}, the soil extractable P, K and Ca, and pH, were linearly correlated to the ash application rate. However, only 18 and 35% of K was extractable after incubation with two acidic soils for 60 days, compared to 63 and 76% of conventional fertilizers. Calcium availability was more favorable, with 44 and 47% of Ca being extractable after 60 days compared to 49 and 58% for limestone.

Erich (1991) and Ohno (1992) showed that the availability of K in wood ash was similar to that of conventional fertilizer.

Campbell (1990) suggested that ash-induced pH and nutrient increases may result in a competitive advantage for hardwoods over coniferous species because hardwoods have higher pH requirements (Pritchett, 1979) and have higher requirements for K, Ca and Mg (double) than coniferous forests (Cole and Rapp, 1981). Tree growth increases in most forests however were attributed mostly to increases in soil K, P and B availability (Etiegni et al., 1991; Ferm et al., 1992; Silfverberg and Hotanen, 1989; Steponkus, 1992). In our case, greenhouse studies showed that wood ash provides the micronutrients, Ca, Mg and K and improves slash pine (*Pinus elliottii, L*) growth. When N, P and K were supplied, the aboveground biomass production was the same as that of plants supplied with commercial fertilizers (Chirenje and Ma, 1999). Erich and Ohno (1992a) showed that the plant (*Zea mays*) uptake ratios of P varied from 0.28 and 0.70 for ash applied to eight different soils.

Liming Effect

Increases in pH of forest soils due to ash application have been shown to be small in many cases (<1), although some studies have shown changes of up to two units (Ferm et al., 1992; Unger and Fernandez, 1990; Weber et al., 1985) using low application rates ($\leq$112 Mg ha^{-1}). The effectiveness of ash in increasing soil pH depends not only on its neutralizing capacity, defined by its CCE, but also on soil chemical and physical properties such as exchangeable Al, CEC, base saturation, texture, and organic matter

(Khanna et al., 1994; Rowell, 1988). All these properties contribute to the soil's capacity to buffer against pH increases.

Because of this liming quality, most researchers have proposed that when its CCE is known, wood ash may be used as an effective liming agent (Ohno and Erich, 1992). In fact, about 11 million Mg of ash are sold annually in the United States as lime and in 1993 this had a monetary value of $58 million (Tepordei, 1993). The average application rate of these ashes was approximately 40 Mg ha^{-1} (remarkably different from the application rates used in this study where the company involved wanted to dispose as much ash as they could on the smallest area possible). There is an advantage of using ash as a lime because a potentially money-draining by-product is turned into a useful and potentially profit- making product.

Improvement of Soil Physical Properties

Wood ash impacts soil physical properties such as porosity, pore size distribution, and conductivity, because it is comprised primarily of silt and clay-sized particles. Studies on the impact of fly ash on soil physical properties have shown increases in soil water holding capacity (WHC) from 12% in the controls to 25% in sandy soils amended with 30% ash (Sims et al., 1995). Amendment of coarse textured soils with coal ash increased WHC from 20 to 33% in two California soils and from 24 to 94% in British soils with application rates ranging from 250 to 1200 Mg ha^{-1} (Chang et al., 1977; Salter et al., 1971). However, the results from coal ash application may not accurately predict the changes in physical properties in soils amended with wood ash. Hence the effects of wood ash on soil physical properties were investigated in this study (Chapter 3).

Concerns Over Land Application of Wood Ash.

The adverse effects of wood ash on soils and groundwater are not well known. These effects have not been studied very well because most researchers apply very low (agronomic) rates of wood ash and most previous research on trace metal contamination of soils mainly focused on sewage-sludge amended soils. In fact, Campbell (1990) suggested that the potential hazard to soil posed by changes in pH and salt concentration are more of a concern than trace metals when applied at low rates. That is why the effects of high-rate application of wood ash on trace metal accumulation and leachability were investigated in this study.

Elevated pH

When wood ash is applied at very high rates such as those investigated in our research (900 to 1800 Mg ha^{-1}), soil pH significantly increases, which can adversely affect plant growth. High pHs reduce the availability of some plant essential nutrients (e.g. P and N) and micronutrients (e.g. Fe, Mn, Mo, Zn) and affects other soil chemical and biochemical reactions essential for rhizosphere organisms. Both the health and diversity of rhizosphere organisms are intimately linked to plant health and growth (Brady and Weil, 1996). Higher pH also leads to solubilization of organic matter and has a negative impact on soil biota. Dissolved organic carbon (DOC) complexes with metals (Buffle, 1988; Lafrance et al., 1989; Sauve et al., 1997) from ash and increases their mobility. Solubilization of organic matter also removes a very important sink of metals in

the soil and mobilizes colloids that may enhance metal transport or at least increase soil solution concentration of trace metals.

A considerable number of studies have shown that wood ash reacts faster with soil than agricultural lime (Clapham and Zibilske, 1992; Muse and Mitchell, 1995). This results in greater initial pH increases that decrease drastically after short periods. Reducing soil pH to more acceptable levels for tree growth and reduction in organic matter solubilization via acidification is a possible solution. This was the basis of our acidification study (Chapter 5).

Excessive Loading of Trace Metals

When wood ash is land applied at high rates, the potential for trace metal contamination also increases. This is a result of two factors: (i) large doses of ash provide high rates of trace metals, and (ii) changes that are associated with high volume application (high pH) increase the solubility of ash and consequently, the potential leachability of ash constituents. Metals were investigated in this research because of the large volumes of wood ash that were applied per unit of soil and hence the higher potential for soil loading and groundwater contamination. The soils in the region where the study was carried out (North Central Florida) are also very sandy with very low organic matter, hence they have lower retention capacity for trace metals. This, coupled with the generally high annual rainfall of the region, could facilitate the movement of trace metals to the groundwater.

The environmental and health impacts of trace metals have been well documented (Adriano, 1986; Bartlett and Kimble, 1976a; Bloom, 1981; Davis, 1984; Manahan, 1991;

Sparks, 1995). Many trace metals have been shown to be carcinogenic, teratogenic and/or mutagenic in human beings (Alloway, 1990; Kurzel and Cetrulo, 1981). Aquatic and soil biota and fauna are also prone to these effects. Eight metals (As, Cr, Cu, Cd, Mn, Ni, Se and Zn) were monitored at different stages of our investigation. Of these eight, As, Cd, Cr and Se have been deemed possible carcinogens by the United States Environmental Protection Agency, USEPA (Manahan, 1991). All except Cu and Mn, have been shown to be toxic to plants and animals at high levels. Copper and Mn have to be present in excessively high concentrations to be phytotoxic. Kurzel and Cetrulo (1981) reported that, of all classes of compounds, metals have the greatest potential for embryotoxicity and teratogenicity. In particular, Cu, Cd, Ni, Se and Zn have been linked to increased abortions and other related birth defects in laboratory mice.

It is nonetheless, important to note that some trace metals, like Cu, Cr, Zn, Ni, and Fe are also essential for microbial, plant and animal nutrition (Adriano, 1986). They are mostly required in enzyme systems where they are involved in energy and electron transfer, processes that are critical for upkeep of life (Alloway, 1990).

When metals are introduced to soil, they usually undergo retention onto exchange sites of organic/inorganic solids, occluded in, or fixed onto soil minerals, taken up by the biological component (Mattigod et al., 1990) or in our case, dissolved in soil solution or precipitated with other compounds in the soil. Understanding the processes governing the accumulation, migration and plant availability of these chemical elements in the soil is, hence, essential for predicting the environmental impact of spreading wood ash on land. Chapters 4, 6 and 7 explore processes that may further our understanding of the effect of land application of boiler ash.

Trace Metal Movement in Soils

Many column studies have been conducted in the last twenty years to study the mobility of trace metals in soils (Camobreco et al., 1996; Madrid and Diaz-Barrientos 1998). However, these studies have mainly focused on soils with very low volumes of amendments. Only a few studies have investigated the release of trace metals from wood ash amended soils and their potential to pollute groundwater. Even fewer studies have investigated the leachability of oxyanions under conditions of extremely high pH and salinity.

Trace metal studies have generally focused on accumulation in soils, plant uptake (and subsequent bioaccumulation in the food chain) and groundwater contamination which has more direct impact on humans (if groundwater is the main water source). The environmental hazards derived from trace metals are closely linked to their solubility and movement in soils. Factors that affect the solubility of metals in ash and metal availability for plant uptake include soil pH, soil CEC, and the amounts of organic matter and hydrous Fe, Al and Mn oxides found in the amended soil (Oden et al., 1993). Other factors e.g. annual rainfall, land management practices, vegetation and fauna, and metal loading rate also play a considerable role (Li and Shuman, 1996).

Soil organic matter plays an important role in the retention and transport of trace metals in soils because of the tendency of transition metal cations to form stable complexes with organic ligands and the significant impact of organic matter on the CEC of the soil (McLaren and Crawford, 1973; Stevenson, 1994). The role of organic matter and colloidal complexation of metals as well as the transport and dispersal of these complexes in the

subsurface has been demonstrated by many authors (McCarthy and Zachara, 1989; Puls and Powell, 1992; Sheppard et al., 1980). In contrast to a simple exchange phenomenon where retention is determined by valence and ionic radius, the selectivity by organic matter depends on the specific electrochemical and structural properties of the ligand and metal ion. Stevenson (1994) suggested that the four mechanisms involved in humic substance adsorption were (1) physical adsorption, (2) electrostatic attraction, (3) hydrogen bonding, and (4) coordination complexes.

Among other things, our study sought to highlight the differences in solubility and leachability of cationic metals and oxyanions using different leachates. Copper and Ni were the cations chosen and As and Cr were the oxyanions studied.

Copper was chosen because of its abundance in the ash and its well-documented association with soil organic matter (Kuo et al. 1983; McLaren and Crawford, 1973; McBride, 1995; Stevenson, 1994). Copper is also of environmental consequence because it generally reacts with organic matter by forming stable coordination complexes rather than by forming compounds via hydrogen bonding or electrostatic attraction. This is mainly due to its low hydration energy and low charge (Stevenson, 1994).

Nickel was chosen because of its presence in high concentrations in the ash and its high association with various soil exchange sites (exchangeable Ni). This is why Ni distribution in profiles of many different soil types is fairly uniform. Nickel is also usually more mobile in soil than the other metals found in ash ($Cd \geq Ni > Zn >> Cu$, Tyler and McBride, 1982) at pH values between 3.8 and 7.1. This increase in mobility is often a result of competition between Ni and Ca for sites on soil colloids (Bowman et al., 1981; Bowman and O'Connor, 1982). Because Ca exists in larger concentrations than Ni in

soils, Ni sorption is significantly minimized. The presence of very high concentrations of Ca in our study had potentially significant implications on Ni adsorption and desorption.

Chromium was studied here as an oxyanion because its only common stable cationic form, Cr (III), is not very mobile under normal conditions (Shupak, 1991). The more mobile and toxic Cr (VI) does not exist as a free ion but as chromate (CrO_4^{2-}), dichromate ($Cr_2O_7^{2-}$), or chromium trioxide (CrO_3) which all behave as divalent anions rather than hexavalent cations (Kimbrough et al., 1999).

The other oxyanion studied, As, was present in low concentrations in the ash but was present in large enough concentrations in the groundwater to warrant concern. Arsenic has also been shown to associate with organic matter (Cullen and Reimer 1989; Xu et al., 1991). Other studies have shown that As leaching from soils is generally limited by adsorption on Fe and Al oxides and clay surfaces, just like P. This is due to the near similarities of the pKas of their respective acids of As(V) and P (successive pKas for H_3AsO_4 at 25°C are 2.2, 6.9 and 11.5, and values for H_3PO_4 are 2.2, 7.2 and 12.4 [Cullen and Reimer, 1989]). This complexity in As chemistry provided an opportunity to understand its behavior in our system.

While most of the factors that affect the solubility and availability of metals from ash apply equally in the dissolution and leachability of oxyanions, their effect may be opposite due to the differences in charge in these species. The conditions under which these factors are most predominant also vary due to charge differences.

Impact of Ash on Soil Chemical Properties

Organic Matter

The high pH associated with the large amounts of wood ash applied in the current study make organic-matter-facilitated contaminant transport a potentially significant mechanism for the conveyance of many low solubility and surface reactive "cationic metals" and metal compounds. This was the driving force behind our investigation to gain a thorough understanding of the mechanisms governing colloidal mobility in aqueous porous media like the one used in this study.

The chemical nature of organic matter has not yet been fully characterized, but it is generally accepted that the fulvic acid fraction of soil organic matter reacts strongly with some metals (Schnitzer, 1969). Schauberg et al. (1980) suggested that the fulvic acid fraction that reacted with metals in sewage sludge amended soils resembled that from natural soil organic matter more than that extracted from sewage sludge.

Insoluble organic matter effectively inhibits plant uptake of those elements which bind strongly with organic matter (such as Cu) and it thereby limits diffusion of these metals to plant roots. In a study of 24 British soils, McLaren and Crawford (1973) concluded that the majority of "available" Cu exists in an organically-bound form. Soluble organics on the other hand raise the carrying capacity of soil solutions for Cu and other metals at certain pHs by forming soluble metal-organic matter complexes (McBride, 1995; Stevenson, 1994). With time, organic decomposition rates and levels of soluble organics diminish and total dissolved metals stabilise at lower levels and this has the overall effect of reducing metal bioavailability.

Effects on Colloids

The relationship between colloidal transport and the dispersal of contaminants in subsurface soil is increasingly becoming more important in environmental research (Corapcioglu and Jiang, 1993; McCarthy and Zachara, 1989; Mcdowell-Boyer et al., 1986; Puls and Powell, 1992; Sheppard et al., 1980). In fact, large proportions of vital and toxic compounds in aquatic systems (surface water, sediment, soil, groundwater and oceans) are associated with colloids. Colloids are frequently operationally defined. For this study, they are defined as organic and inorganic entities in size range from 0.001 to 1μm (Buffle and Leppard, 1995a,b). Frequently encountered colloidal constituents include microorganisms or biological debris, iron (oxy)hydroxide, calcium carbonate, secondary phyllosilicates, amorphous silica, polysaccharides or organic fibrillar material, gel-like organic material and soil-derived fulvic compounds.

The shape of natural colloids is much more complex than that of spheres and smaller colloids and their aggregates with macromolecules are very porous. The specific surface area of colloidal material in the smaller size ranges is generally very high. For example, the specific surface area of colloids in the size range 1-450 nm is equal to or larger than that of particles in the range 0.45-100μm. Peret et al. (1994) showed that 40 to 70% of the total area in a Rhine river samples was due to colloids <200nm despite the fact that this fraction only accounted for 1.5% of the total mass.

Because colloidal materials of biological and geological origin are ubiquitous in natural aquatic environments (O'Melia, 1990; Stumm, 1993), colloid facilitated contaminant transport is a potentially significant mechanism for the conveyance of a variety of low-flow velocity, low solubility and surface reactive compounds in subsurface

soil including radionuclides (Penrose et al., 1990; Sheppard et al., 1980), metals (Jardine et al., 1989; Puls and Powell, 1992), and hydrophobic organic compounds (Bellin and Rao, 1990; Jardine et al., 1989; Kan and Tomson, 1990; Linqvist and Enfield, 1992).

The extent of colloidal transport in groundwater is dependent on the rate at which the colloidal particles deposit onto stationary mineral grain surfaces. This deposition in itself is a dynamic process governed by variable kinetics (Johnson and Elimelech, 1995; Ryde et al., 1991; Song and Elimelech, 1993). The rate depends on a variety of factors including solution chemistry and the chemical characteristics of the colloid and collector grain surfaces (Johnson and Elimelech, 1995; Ryde et al., 1991; Song and Elimelech, 1993). Also, just because a contaminant is associated with colloids in groundwater, this does not mean that its transport was facilitated by colloids. The association may have happened after the contaminant had reached groundwater.

Characterizing the nature and behavior of natural colloids and macromolecules is a complex task. It requires the appreciation of the factors behind processes like coagulation-sedimentation (dependent on size, density, compactness, rigidity and chemical processes of the surface), chemical processes and microbial activities, and sophisticated mathematical modeling. Under natural field conditions, the colloidal composition of surface water results from the steady state between inputs and outputs that are continuously operative through physical, chemical and microbial actions while in a removed system (samples), the open aquatic system is suddenly closed. The large application rates used in this research were expected to change colloid dynamics in the natural forest system, hence the need to look at change in colloid behavior after ash application.

Solution Ionic Strength

Solution salinity affects the solution ionic strength and a plethora of other chemical reactions. Daylin et al. (1995) suggested that ionic strength influences the dynamics of colloidal deposition and transport (in our case, mostly organic matter-metal complexes) in heterogeneous porous media by controlling the range and magnitude of interparticle forces. The presence of specifically interacting divalent counterions at moderate concentrations in soil solutions promote interparticle attraction. This in turn increases deposition rates as particles retained on the stationary mineral grains act as additional collectors.

The surface area blocked by a particle deposited on a spherical collector increases as the ionic strength is reduced and is generally several times larger than the projected area of the particles. Variations in the magnitude of the excluded area may be in part responsible for the release (mobilization) of colloidal particles from stationary mineral grain surfaces that is commonly observed following a reduction in ionic strength. A reduction in ionic strength produces an expansion of the electric double layer surrounding charged colloid particles, thereby causing repulsion between particles deposited on favorable patches and reduction in the maximum attainable surface coverage corresponding to a monolayer of deposited particles. The high salinity of the samples in this study has significant implications on this relationship.

Summary

Many studies on different types of wood ashes all suggest that ash can be a good source of nutrients and a liming material. All studies evaluated dealt with very low

application rates. However, due to the increases in the amount of ash being produced lately, some companies have explored using high application rates on land. The question is, is this feasible and if it is, what are the factors that ought to be considered before application? This study was done on a sandy soil with very low organic matter and the soil is located in a very high rainfall area. The results that we are going to get will be applicable under many situations because our conditions generally represent the worst case scenario in land application of ash. The study in no way advocates the land application of excessive amounts of waste for any purpose. The study was done to understand the processes that are happening in one such worst case scenario.

CHAPTER 3
IMPACT OF HIGH-VOLUME WOOD ASH AMENDMENT ON SOIL PROPERTIES AND NUTRIENTS

Introduction

Land application of wood ash changes nutrient cycling. This change results from direct nutrient addition, changes in pH dependent soil chemical equilibria (Davies and Jones, 1988; Wild 1988), microbial decomposition of organic matter (Fritze et al., 1994; Khanna et al., 1994; Weber et al., 1985) and related chemical and biochemical processes. Addition of wood ash to soil has been shown to improve soil fertility and physical properties of coarse textured soils when applied at agronomic rates (Erich and Ohno, 1992a; Naylor and Schmidt, 1986; 1989). Wood ash application supplies Ca, Mg, K, Cu, Zn, Fe, and Mn, all of which are essential plant nutrients. The N and S (and sometimes P) contents of wood ash are low because these elements are volatilized from plant biomass upon combustion (Mitchell and Black, 1997). Wood ashes are good sources of Ca, K and Mg as well as other nutrients that are removed when trees are harvested in intensively managed forests (Federer et al., 1989; Hornbeck et al., 1990). The availability of these elements is also dependent on the rate of dissolution from ash and the subsequent reactions with the soil (Ohno, 1992). In a study on the effectiveness of wood ash in

supplying plant essential nutrients, Naylor and Schmidt (1986) showed that increases of soil extractable Ca, Mg, K and P were linearly correlated with ash application rate.

Because of its fine texture, wood ash has the potential to improve the water holding capacity (WHC) of coarse textured soils (Sims et al., 1995). Various studies have shown WHC increases between 20 and 94% after application of coal fly ash at rates ranging from 250 to 1200 Mg ha^{-1} (Chang et al., 1977; Salter et al., 1971). In most soils, increased water holding capacity increases the range over which water is available for plant uptake and reduces the amount of energy plants have to spend to extract water from the soil. However, high ash application rates are needed for these benefits to be realized and applying ash at high rates leads to potential problems with salinity and high pH. This study seeks to determine the effects of boiler ash on the physical properties of our soil and weigh any benefits against the potential problems of using high rates.

Wood ash generally has an alkaline pH and is high in salts. Thus, addition of high rates of wood ash may have an adverse impact on soil by elevating soil pH (causing some nutrients e.g. P to exist in unavailable forms for plant uptake), increasing soil salinity and raising soil trace metal concentrations (increasing the risk of micronutrient toxicity). However, when used properly, wood ash can be a valuable liming material (Muse and Mitchell, 1995). In our study, high application rates were studied because the company that was disposing of this ash had already decided these rates (with the intention of increasing moisture retention) when we got involved in the study. Therefore this is a study of a worst case scenario meant to get the best out of a bad situation.

The purpose of this monitoring study was to determine the effect of high volume boiler ash application on the productivity of forest soils by 1) evaluating changes in soil

chemical and physical properties after ash amendment; and 2) investigating the effects of the rates and methods of ash application on the availability of plant nutrients and their mobility in soil.

Materials and Methods

Site Preparation and Treatments

The soil at the site used for this study was an acidic fine sand (Typic Quartzipsamment) with a spodic horizon below 2 m. The site (located in Hawthorne, Florida; Fig. 3-1) was cleared and de-stumped from September to October, 1995. Boiler-ash was hauled to the site in November of the same year and the spreading and mixing of the ash was completed in December, 1995. A split-plot design was used with surface and subsurface treatments as main plots, each plot having an area of ~0.21 ha (Fig. 2-2). Wood ash was applied to the surface plots at rates of 0, 900 and 1800 Mg ha^{-1} on the surface and incorporated to a depth of 47 cm. This was the maximum depth accessible with the equipment used to mix the soil.

The initial rationale for using these excessively high rates was to improve moisture retention of this sandy soil with little attention being paid to the potential impact on soil chemical properties. This was in the wake of the uneven distribution of rainfall at this site which experiences short lived torrential downpours in the summer and long dry winters (Fig. 3-3a). This apparently fit well with the company's objective to dispose of the largest possible amount of ash with the least possible cost. That is why this study carried out as a worst case scenario.

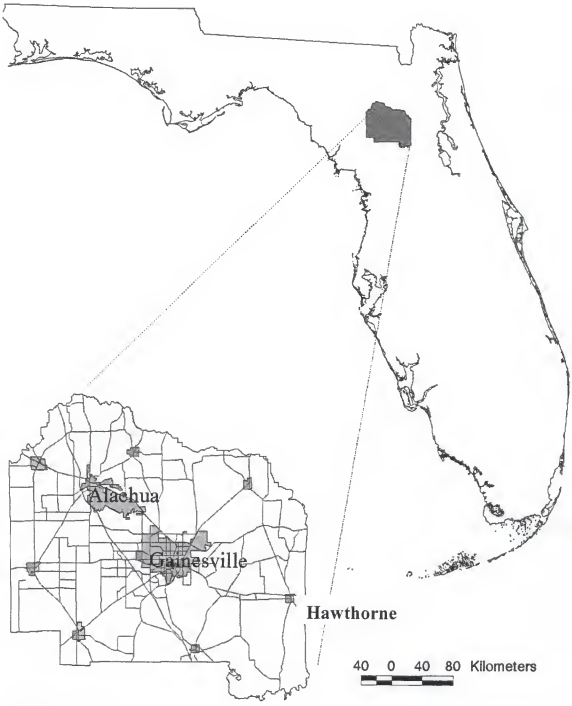


Figure 3-1. The location of the field monitoring site in Hawthorne (the site is actually just across the border in Putnam County). Source: Gerco Hoogeweg, Soil and Water Science Department, University of Florida.

Subsurface plots (top 0.5m of soil was scrapped off before ash application/incorporation)

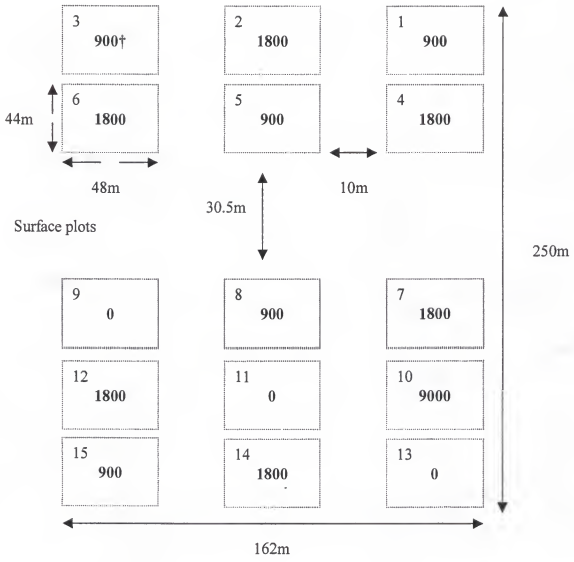


Figure 3-2. The layout of plots used in our study.

† The application rates were in Mg ha^{-1}
Each plot had an area = 44m x 48m = 0.21 ha
Total area of plots = 162m x 250m = 4 ha
Two monitoring wells were installed in each plot for a total of 30 wells

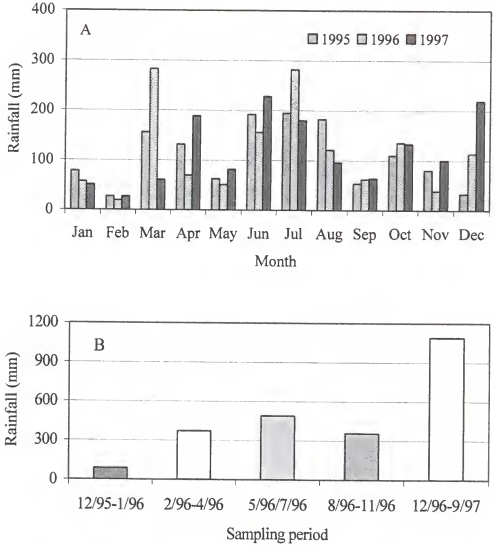


Figure 3-3. Rainfall patterns at the site (a) distribution in the last 3 yr and (b) total rainfall that fell within sampling periods

For the subsurface plots, the top 50 cm of soil was removed and ash was applied at 900 and 1800 Mg ha^{-1} and incorporated to a depth of about 47 cm. The topsoil in the subsurface plots was then put back (after 18 months) prior to planting of slash pine seedlings in July of 1997. The total area of the 15 research plots (5 treatments x 3 replicates) was approximately four hectares.

A total of five samplings were conducted. Soil samples were initially collected quarterly (1/29/96, 4/29/96, and 7/25/96) from six depths (0-20cm, 20-40cm, 40-60cm, 60-80cm, 80-100cm and the spodic horizon, below 2m) in each research plot. Later, samplings were made after six and nine months (11/12/96 and 09/17/97). Three sub-samples from three spots in each plot were collected using a calibrated auger and mixed to obtain composite samples. Selected chemical and physical properties of the ash and soil used in this study are shown in Table 2-2.

Analyses of Soil Physical Properties

Moisture characteristic (volumetric water content versus suction) curves for the control soil and treated plots were determined from soil core samples collected from the field in January of 1997, ~13 months after the ash application. The cores were placed in initially water-saturated Tempe cells and subjected to stepwise increases in suction from 0 (saturated) to 350cm. They were then transferred to a pressure chamber and subjected to 15 000cm of suction (dry). Gravimetric moisture content was determined for the cores after 48 hours of equilibration at each suction. Saturated hydraulic conductivity was determined by letting water flow freely through a 10 cm long saturated soil column, and collecting and measuring the volume of the leachate per unit time. Bulk densities were determined by measuring the weight of soil in the Tempe cells and dividing it by the volume of the cells.

Chemical Analyses

For total elemental concentrations, samples were air-dried and digested in a CEM MDS-2000 microwave digestion oven using the United States Environmental Protection

Agency (USEPA) method SW846-3051 (USEPA, 1986). Specifically, 0.5g of air dry soil were digested in 10 mL concentrated nitric acid and made up to 100 mL with nanopure water. Plant extractable or available macronutrients (Ca, Mg and K) in the soil were extracted with 1M ammonium acetate (NH_4OAc) at pH 7 (Schollenberger and Simon, 1945). Plant extractable micronutrients (Fe, Mn, Zn, and Cu) in the soil were extracted using DTPA solution (Haq and Miller, 1972). Concentrations of total As, Cr, and Se in the ash and soil were determined using a Perkin Elmer SIMAA 6000 graphite furnace atomic absorption spectrophotometer and those of all other elements using a Thermo-Jarrell-Ash 61E Inductively Coupled Argon Plasma Atomic Emission Spectrophotometer (ICAP-AES). The spike recoveries for all elements were within 80 to 120% and the quality control samples were all within 10% of the known values. The pH and electrical conductivity were determined using an accumet model 20 pH/conductivity meter (Fisher Scientific). The total organic carbon was determined on a Shimadzu TOC 5050 carbon analyser. The ash sample was also analyzed by x-ray diffraction. The CCE of the soil was determined using the method described by Erich and Ohno (1992a). All statistical analyses were carried out using analysis of variance in Statistical Analysis Software (SAS Institute 1982).

Results and Discussion

Most research on the impact of wood ash application on soil properties deals with relatively low application rates, i.e. <50 Mg ha^{-1} (Mattigod et al., 1990; Naylor and Schmidt, 1989; Williams et al., 1995). Increased nutrient levels in ash-amended soils

have nonetheless been observed at these low rates (Campbell, 1990; Ohno and Erich, 1990). Therefore, significant increases in elemental concentrations were expected as a result of the high rates of ash application in this study.

An important consideration in this study was the heterogeneity of the ash samples and the size of the experimental plots. The ash used was accumulated in a heap by the company over a period of three years. Although the ash used for this study was taken within one week, samples taken from that heap could vary according to age, batch differences due to temperatures of combustion and type of wood, and influence of external weather conditions (e.g. rainfall leaches nutrients). Minor variations in concentrations of Cr, As, Se and Mn were observed in ash from different batches.

The plot size of 0.2 ha was also large enough to cause significant variation within each plot. Although subsampling of soil was done within each plot, application of large quantities of ash using heavy equipment resulted in heterogeneity within the same treatments, which is expected for this type of field operation. This heterogeneity was reflected in large standard deviations observed in my data.

In this study, soil samples were taken from six depths (down to the spodic horizon), but only data from the surface soils (0-20 cm) in both application methods (surface and subsurface) are discussed in this chapter (data from the lower horizons are discussed in chapter 4). The boiler ash was mixed with the surface soil, thus the surface soil in both the surface and subsurface treatments was most impacted by the ash.

Changes in Soil Properties.

The most significant changes in soil properties were in pH, electrical conductivity and water holding capacity ($p < 0.05$). The magnitude of change in these properties was particularly high in our case because of the very high application rates used.

Soil pHs ranged from an average of 5.6 in the control plots to above 9.5 for all treatment plots, representing an increase of at least four units (Fig 3-4a). This was expected since large amounts of boiler ash of extremely high pH (11.4) were applied to the soil (Table 2-2). Such drastic changes in soil pH are not unprecedented. Ulery et al. (1993) reported increases of up to three units in their study of an intensely burnt field site and Cass et al. (1984) reported pH increases of up to 5 units after burning in surface soils. There were no significant differences in pH between soils receiving application rates of 900 and 1800 Mg ha^{-1} in our study. It took up to eight months for the Bh horizon (located at > 2m below surface) to reach pH levels close to those of the surface soil in our study (data not shown). The Bh horizon contains more colloidal materials than the overlying soil horizons, making it more resistant to changes (higher buffering capacity) in pH than other horizons. Surface soil pH decreased from above 9.5 to around 8.6 after seven months for all treatments at the site mainly due to leaching of the easily leachable K and Na carbonates which buffer pHs at very high values (Fig. 3-4a).

The pH of the boiler ash used in this study was more than twice that of unamended soil (Table 2-2). The ratios of Na, K, Ca and Mg in the ash to that of soil were 650, 267, 190 and 10 respectively (Table 2-2). Therefore, considerable leaching of alkaline-earth and alkaline metal salts in the ash was required to decrease soil pH and salinity. The solubilities of the predominant carbonates in the ash are 0.014 g $CaCO_3$,

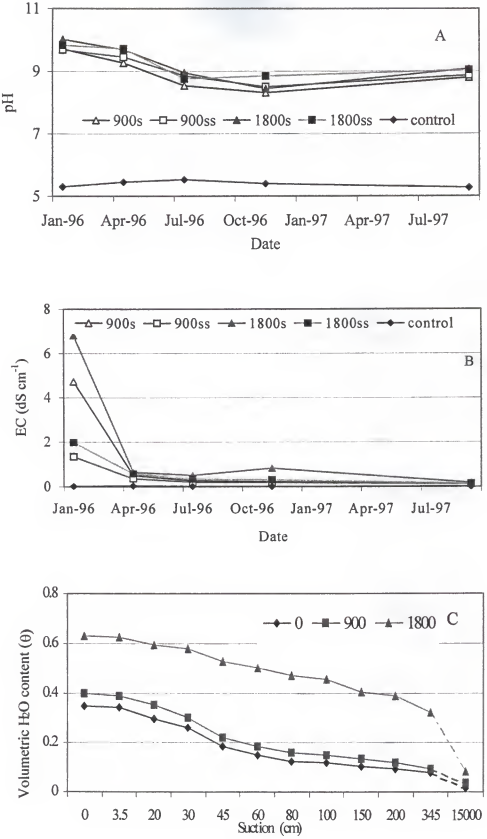


Figure 3-4. Variation of (a) pH (b) EC with time and (c) water content with suction in the different treatments (s-surface, ss-subsurface).

0.106 g $MgCO_3$, 71 g Na_2CO_3 and 1120 g K_2CO_3 per liter of cold water (Lide, 1991). Taking 1300 mm as the average annual rainfall for the site (Fig. 3-3a), it would take at least two and half years to leach all the $CaCO_3$ from the soil assuming no protection of carbonate by soil particles. Sodium and K carbonates leached out within considerably shorter period due to their higher solubilities.

The pH of the surface soil decreased and stabilized at approximately 8.6 after the initial seven months (Fig. 3-4a) due to the presence of $CaCO_3$. This is consistent with our expectations because the more soluble K and Na carbonates had been leached out by then. There was very little change in pH in the subsequent 14 months ($p > 0.05$) showing that the $CaCO_3$ was still present in the soil in large quantities (~10%). Soil clay and organic matter generally protect carbonate from dissolution. From these soils, the time it takes for the carbonates to leach out completely tends to be much longer than the theoretical prediction (Hatch and Pepin, 1985; Etiegni et al., 1991). The pH of 8.6 is too high for optimum slash pine (the species usually grown at this site) growth. Prior to planting, an acidification treatment with materials like sulfur may be required to neutralize the ash. To avoid excess alkalinity, the ash should therefore be applied based on calcium carbonate equivalent (CCE, 20%).

In addition to pH concerns, the change in EC value must also be considered since high EC values (indicating high salt content) reduce a plant's ability to take up water and assimilate nutrients. In this study, the electrical conductivity (EC) in the surface soil increased by up to two orders of magnitude in all treatments (8.6 to 9 dS cm^{-1} compared to the control of 0.02 dS cm^{-1}), indicating significant accumulation of soluble salts in the soil (Fig. 3-4b). However, up to 50 times reduction in EC in the surface soil was

observed after only four months of leaching (<500mm rainfall, Fig. 3-3b). Sodium and K salts are very soluble and thus leached out quickly, resulting in significant reduction in EC (K decreased from 700 to < 200 mg kg^{-1} in the 1800 Mg ha^{-1} treatments).

At the end of the monitoring period, the surface soils still had up to 18 times the EC of the control (0.37 dS cm^{-1} in the 1800 Mg ha^{-1} surface treatment compared to 0.02 dS cm^{-1} in the control). The EC values of the lower parts of the profile were up to three times higher than those of the surface at the end of the study (21 months), indicating that the salts were still migrating through the soil (data not shown). Other researchers have also noted reduction in EC and pH after pre-leaching samples with significant amounts of simulated rainfall prior to greenhouse studies (Ghodrati et at., 1995) or by leaching with pore volumes equivalent to 18 months of rainfall in Marriot columns (Sims et al., 1995). The high leaching rate of salts lowers soil salinity and hence improves plants' ability to take up nutrients and water.

Organic matter content was greater in the surface horizons than the controls ($p < 0.05$; data not shown). This may have been due to the contribution of carbon from ash (25% organic matter; Table 2-2). Higher organic matter content improves soil physical (moisture retention and soil temperature et cetera) and chemical properties (improved CEC and nutrient supply) hence enhancing tree growth.

The Bh horizons in the 1800 Mg ha^{-1} treatments underwent visual bleaching (light color) during the leaching process while those in the 900 Mg ha^{-1} treatments did not. The high pH induced by ash in the high rates (at lower depths) was responsible for the dissolution of the organic matter from the spodic horizon in the higher treatments. Groundwater collected from these plots was dark colored indicating the presence of large

quantities of organic matter (see Chapter 4). The Bh horizons in the subsurface treatments had more bleaching because the alkaline leachate in these plots traveled shorter distances (50 cm shorter) to reach the Bh horizon and hence there was less dilution by the soil. Profiles in the subsurface plots did not have the A horizon which generally also has fine sized constituents that buffer against changes more so than the subsurface layers. Concentrations of dissolved organic carbon (DOC) in groundwater samples collected

Table 3-1. Total (nitric acid extracted) and available (ammonium acetate and DTPA extracted) elemental concentrations in the soil amended with different rates of ash at the beginning and end of the study (mg kg^{-1})

Element	Surface plots				Subsurface plots			
	900 Mg ha^{-1}		1800 Mg ha^{-1}		900 Mg ha^{-1}		1800 Mg ha^{-1}	
	0	21 month	0	21 month	0	21 month	0	21 month
	Total concentrations							
Ca	6190	3030	14200	6390	7140	2520	12660	4330
Fe	1100	1100	1700	1600	1100	1000	1600	1500
Mg	660	340	1410	1400	570	290	1220	460
K	390	130	740	230	390	100	700	160
P	380	160	550	260	230	110	400	170
Mn	50.0	20.0	100	30.0	100	30.0	100	60.0
Zn	20.0	10.0	40.0	20.0	10.0	10.0	30.0	10.0
Cu	1.00	2.00	4.00	4.00	1.00	6.00	1.00	7.00
	Available concentrations							
Ca	290	320	310	440	280	260	370	390
K	56.0	18.0	120	43.0	25.0	9.30	50.0	27.0
Mg	7.30	10.0	12.0	16.0	4.70	6.10	9.40	13.0
Fe	11.0	3.10	20.0	3.90	4.10	3.40	5.10	2.30
P	2.30	1.60	6.60	2.30	1.70	1.20	2.60	1.60
Mn	2.30	0.70	2.40	2.20	1.10	0.80	1.70	1.30
Zn	1.30	0.50	2.70	1.00	0.60	0.40	1.40	0.50
Cu	0.30	0.20	0.50	0.50	0.10	0.10	0.30	0.30
PH	9.70	8.80	10.0	9.10	9.70	8.90	9.80	9.00
EC (dS m^{-1})	4.70	0.14	6.80	0.18	1.30	0.12	2.00	0.14
OM (%)	0.90	1.90	1.10	3.30	0.40	1.10	0.60	1.80
K_h (cm h^{-1})	18.8		8.60					
ρ_b (g cm^{-3})	1.36		1.23					

from the soil of the 1800 Mg ha^{-1} plots support this observation. For the first 6 months, an average of 600 mg/L of DOC was observed from the subsurface plots compared to 300 mg/L in the surface plots (data not shown).

In terms of physical properties, wood ash increased the soil's WHC significantly ($p < 0.05$) at all suctions evaluated (Fig 3-4c). For the soil alone, the moisture content between field capacity and permanent wilting point (100 to 300 cm suction) was between 8 and 14% (6% plant available water). The corresponding values for the ash treated soils were 10-16% (6% plant available water) and 30-42% (12% plant available water) in the 900 and 1800 Mg ha^{-1} treatments respectively (Fig 3-4c). Under typically dry soil conditions (above 300 cm suction), the ash-treated soil contained 10 to 30% moisture compared to < 8% for the control. Ash therefore increases the chances of plant survival under conditions of extended water stress in soils. The finer texture of the ash increased total soil porosity and changed the pore size distribution of this predominantly sandy soil from mainly macropores to a larger percentage of meso- and micropores which retain more water under typical soil conditions (Table 2-2). The increase in soil WHC for the 900 Mg ha^{-1} treatment did not translate to more plant available water, however, because only slight changes in the soil moisture characteristic curve were observed for this treatment (Fig 3-4c). However, the increase for the 1800 Mg ha^{-1} treatment led to more plant-available water, because of the greater influence that the larger quantities of finer particles had in this treatment. Ghodrati et al. (1995) also observed an increase in soil WHC and a corresponding reduction in saturated hydraulic conductivity for a soil amended with 20 to 40% (w/w) coal fly ash. These studies clearly show that for any significant increases in WHC to occur, ash has to be applied at very high rates. However,

the benefits in WHC may be overshadowed by the potential negative impacts from application of ash at these high rates.

On the other hand, the saturated hydraulic conductivity of soil significantly decreased ($p < 0.05$) from 28.2 cm hr^{-1} in the controls to 18.8 and 8.6cm hr^{-1} in the 900 and 1800 Mg ha^{-1} surface treatments respectively (Table 3-1). This reduction was the direct result of the reduction in pore sizes induced by the ash, causing water to stay longer in the root zone where it is needed the most. The reduction in saturated hydraulic conductivity was linear within the range of boiler ash application rates used ($r = 0.99$). A decrease in hydraulic conductivity translates into increased water residence time in the root zone where it is needed most.

The dry bulk density of the soil before boiler ash application was around 1500 kg m^{-3}. This decreased to 1360 and 1230 kg m^{-3} ($p < 0.05$) after incorporating boiler ash, which has a much lower density, at rates of 900 and 1800 Mg ha^{-1} respectively (Table 3-1). The decrease in bulk density improves root penetration, soil aeration for both plant roots and microbial communities and improves soil trafficability (Hillel, 1998).

Macronutrients

Calcium, Mg and K are essential macronutrients for plant growth and their increase is beneficial for managed forest systems. Managed forest systems, like our site, continuously lose Ca, Mg and K through harvesting and leaching. Increased base saturation has been shown to have both long-term and short-term nutritional benefits for these systems (Lerner and Utzinger, 1986; Naylor and Schmidt, 1986). Khanna et al. (1994) showed a direct relationship between increased Ca, Mg and K and plant growth

and yield. Other researchers have shown that macronutrients like Ca, K and Mg exhibit differential solubility in ash-amended soils (Ghodrati et al., 1995).

Application of boiler ash at the rate of 900 Mg ha^{-1} represents an application of 1 590, 440, 330, and 12.6 kg of potentially available K, Ca, Mg, and P respectively (Table 2-2). Total Ca (Fig. 3-5a), Mg (Fig 3-5b), K (Fig 3-5c) and P (Fig 3-5d) increased to appreciable levels in all ash-amended soils. The relative increase in total nutrient concentrations was in the order of K >> Ca >> Mg. This was in agreement with Kahl et al. (1996) who observed a similar order one month after ash application in a Spodosol. After 25 months, the order of Kahl et al. (1996) was Mg > Ca > Na, reflecting the lower solubility of Mg and Ca. In our study, the order after 21 months was Ca > Mg > K. The differences in this sequence may lie in the different compositions of the ash used in this study and that used by Kahl and others. Grier (1975) and Khanna et al. (1994) reported that mobilization of elements from ash into soil leachate was in the order of K > Mg > Ca > P, which is consistent with this study.

Total soil Ca concentrations initially increased from 130 mg kg^{-1} (45% available Ca; Table 2-2) to about 6 190 (~ 5 % available Ca, $p < 0.05$) and 14 200 mg kg^{-1} (~ 2 % available Ca, $p < 0.05$) in the 900 and 1800 Mg ha^{-1} surface treatments, respectively (Table 3-1). The subsurface treatments had slightly higher but statistically insignificant ($p > 0.05$) Ca concentrations; about 7140 (~ 4% available Ca) and 12 700 mg kg^{-1} (~ 3% available Ca) in the 900 and 1800 Mg ha^{-1} treatments, respectively (Table 3-1). There was about 25 % reduction in Ca concentration, through leaching, in each of the first three quarterly sampling periods (Fig 3-5a). This was to be expected since $CaCO_3$, the main Ca salt in the ash, is not very soluble. Approximately the same amount of Ca was lost prior

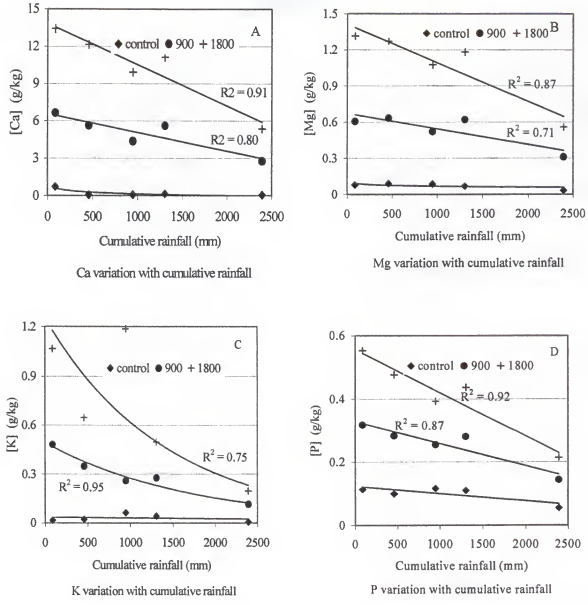


Figure 3-5. Changes in total concentrations of Ca, Mg, K, and P in the upper 20 cm of the surface and subsurface treatments with rainfall after application of boiler ash.

to the first sampling (taken a few weeks after the ash incorporation [88 mm of rain]) as was lost during the following three months (372 mm of rainfall). It took over a year to

reduce the soil Ca concentration by 50 % possibly due to Ca salts reacting with the soil and becoming less soluble. The amount of Ca leached is linearly correlated to the amount of rainfall (Fig. 3-5a). Khanna et al. (1994) observed a similar pattern in Ca and Mg leaching using eucalyptus ash.

Based on Fig 3-5a, it would take a cumulative amount of 4500 mm of rainfall or three years to leach out all the remaining Ca. Our projected value is slightly higher than the calculated value of two and half years using the solubility of $CaCO_3$ because of the reaction between Ca and soil. This reaction may slow leaching even more as Ca concentration in the soil decreases. At the end of 21 months, Ca concentration in the surface soils was still about 30 and 70 times higher for the 900 and 1800 Mg ha^{-1} surface treatments, respectively, than the controls (Tables 2-2 and 3-1). There was very little change in the available Ca in all treatments during the 21 month monitoring period ($p > 0.05$, Table 3-1). The 1800 Mg ha^{-1} subsurface treatment had lost more Ca by the end of the study than the 1800 Mg ha^{-1} surface treatment (Table 3-1). This was possibly due to the presence of higher concentrations of fine particles and organic matter in the surface soils than the subsurface soils.

The initial increase in soil Mg concentration due to ash amendment was directly correlated to Mg concentration in the ash. The ash to soil Mg concentration ratio was 10 (Table 2-2). Total Mg concentration after ash incorporation in the 1800 Mg ha^{-1} treatment was about 1410 (1% available Mg) and 1220 mg kg^{-1} (1% available Mg) in the surface and subsurface treatments respectively (Table 3-1). This was about twice that in the 900 Mg ha^{-1} treatments (700 and 600 mg kg^{-1} respectively). Total Mg concentrations decreased by almost the same factor during the first four sampling periods (Fig 3-5b). At

the end of 21 months, Mg concentration in the surface soil was still about 20 (for the 1800 Mg ha^{-1} treatment) and 10 times (for the 900 Mg ha^{-1} treatment) higher than that of the controls ($p<0.05$; Tables 2-2 and 3-1). The 1800 Mg ha^{-1} subsurface treatment lost more Mg by the end of the study than the 1800 Mg ha^{-1} surface treatment. Ammonium acetate extractable Mg had actually increased 30% at the end of 21 months. This may have been due to the slow initial release of Mg by the ash.

Total K concentrations did not increase as drastically as was expected from the high K concentration in the ash. The ratio of ash to soil K concentration was 267 (Table 2-2). The K concentration initially increased from 50 mg kg^{-1} in the control to about 400 and 700 mg kg^{-1} in the 900 and 1800 Mg ha^{-1} for both the surface and subsurface treatments ($p < 0.05$, Table 3-1). Plant available K in the surface treatments ranged from 14 % in the 900 Mg ha^{-1} treatment to 19 % in the 1800 Mg ha^{-1} treatment. The corresponding values in the subsurface treatment were 6 to 17%. Total K concentration decreased exponentially in the initial stages of leaching (Fig. 3-5c), which was more rapid than for either Ca or Mg. Williams et al. (1996) observed that K leached to a depth greater than any other cations in their field study. At the end of 21 months, K concentration in the treatments had dropped to about twice that of the control in our experiment (Tables 2-2 and 3-1). This represents a loss of at least 60% of the initial K and reflects the high leachability and solubility of K salts. Kahl et al. (1996) also observed very high K leachability in their study.

Although total K in all treatments in our study substantially decreased with time ($p < 0.05$), the proportion of plant available K increased with time ($p > 0.05$, Table 3-1). It is difficult to predict how much rainfall would be needed to leach out all the added K

because other factors relating to soil-K interactions come into play. The final concentration of K in the 1800 Mg ha^{-1} subsurface treatment was much lower than that in the corresponding surface treatment ($p < 0.05$). Khanna et al. (1994) grouped K, B and S together in the highly soluble group in their determination of chemical properties of eucalyptus ash.

There was a five-fold increase in P concentrations in the ash-amended soil ($p < 0.05$). Less than 25% of this P had been lost by the end of the first year (Fig. 3-5d). This may be attributed to the lower solubility of P under conditions of high soil pH. Ohno and Erich (1990) showed that even when P levels were increased, there was not an increase in uptake by plants or improved plant growth because phosphate easily undergoes ligand exchange with hydroxylated mineral surfaces (Goldberg and Sposito, 1985). The low concentrations of plant available P in all treatments (< 0.1 % plant available P; Table 3-1) is a testimony of this. The high concentrations of Ca in our study may have fixed P also as calcium phosphates. The 1800 Mg ha^{-1} treatment had significantly higher P concentrations than the 900 Mg ha^{-1} treatment and the surface treatments had significantly higher P levels than the subsurface (Table 3-1). The presence of fine textured materials in the surface treatments may be responsible for the higher levels of P retained in these layers. Richards and Charley (1983) observed a significant increase in P dissolution when ash was mixed with an acid soil. Phosphate leaching also occurs when all the hydroxylated surfaces have been saturated by P (due to oversupply) and this explains the steeper curve in the 1800 Mg ha^{-1} treatment in our study (Fig. 3-5d).

Micronutrients

Most studies dealing with wood ash applications do not consider micronutrients due to the low amounts of ash applied (< 50 Mg ha^{-1} in most cases; Williams et al., 1995; Mattigod et al., 1990). For example, Kahl et al. (1993) did not observe any change in trace metal concentrations after application of wood ash to a Maine forest soil. Their application rates were considerably lower than the rates used in this study (~ 20 Mg ha^{-1}).

Levels of Mn and Fe (Table 3-1) were significantly elevated following ash application ($p < 0.05$). Manganese concentrations were more than doubled in the 900 Mg ha^{-1} treatments and quadrupled in the 1800 Mg ha^{-1} treatments. There was a higher concentration in the 900 Mg ha^{-1} subsurface treatment ($p < 0.05$) because subsurface soils naturally have higher Mn concentrations than surface soils. There were nonetheless, no significant differences between the two application methods in the higher application rates ($p > 0.05$, 1800 Mg ha^{-1}). This might be due to the exceedingly high quantities of ash that may have masked all soil factors at this high rate. Among the micronutrients, Mn had the highest concentration in the ash (Table 2-2) and it had the highest relative concentration increase. Manganese also had the second highest availability among the micronutrients (after Zn), ranging from 1 to 7%. Manganese concentrations in the ash-amended soils went down to an average of 30 mg kg^{-1} at the end of the study but this was still double the native soil concentrations. The high solubility of Mn in this experiment may be linked to its adsorption on Ca and Mg carbonate surfaces (McBride and Blasiak, 1979) and the dissolution and leaching of $MnCO_3$ at high pH (Mattigod and Sposito,

1977). When the Ca and Mg carbonates were solubilized in our system, any adsorbed Mn was also transported down with the carbonates.

Iron concentrations in the ash-amended soils increased from a background concentration of 800 mg kg^{-1} to 1100 ($p > 0.05$) and about 1700 mg kg^{-1} ($p < 0.05$) in the 900 and 1800 Mg ha^{-1} treatments respectively (Tables 2-2 and 3-1). There were also no significant differences between the two application methods for both ash application rates. There was very little change in total Fe concentration in all treatments at the end of the study. Both Mn and Fe are essential micronutrients for plant growth but they may become toxic to plants at high concentrations (Brady and Weil, 1996). The ash used in this study had very high concentrations of Mn and Fe (Table 2-2). However, Fe precipitates under conditions of high pH such as those used in this study. This is manifested in the very low concentrations of plant available Fe (Table 3-1) and it also explains the low Fe leachability. Precipitation reduces the toxicity concerns that may arise from the presence of high total concentrations from these elements.

Copper concentrations in surface soil did not change except in the 1800 Mg ha^{-1} surface treatment (Table 3-1). Total Cu concentrations had actually increased by the end of the monitoring period ($p > 0.05$), which was unexpected. Twenty to 30 % of this Cu was available for plant uptake but this was not enough to warrant any concerns about toxicity to plants.

The ash to soil ratio of Zn concentration was very high (470; Table 2-2). There was a substantial increase in total Zn concentrations in the surface soil ($p < 0.05$, Table 3-1). Soil Zn concentration in this study increased 10 - 20 times to about 20 and 40 mg kg^{-1} in the 900 and 1800 Mg ha^{-1} treatments respectively ($p < 0.05$). Available Zn

concentrations were also the highest among the micronutrients, ranging from about 4 to 7%. This was in agreement with our expectations from the high percentage of available Zn in the ash and other published results that show that Zn is easily soluble in soil (Juste and Mench, 1992; Henry and Harrison, 1992). Approximately half of the Zn had leached out by the end of the study.

Pot studies have shown that slash pine plants amended with certain wood ashes may not require additional micronutrients for optimum growth (Chirenje and Ma, 1999a; Naylor and Schmidt, 1989; Campbell, 1990). This is important because the essential micronutrients Zn, Fe, Cu and Mn supplied by ash are taken up by plants to meet their nutritional requirements during growth and an ash application cycle can be developed whereby ash is applied after the added nutrients have been depleted.

Conclusions

Addition of boiler ash improved soil physical properties by increasing plant available water, reducing saturated hydraulic conductivity and improving tilth through reduction of bulk density in this sandy soil. In addition, ash significantly increased total and available soil macronutrients (Ca, Mg, K, and P) and micronutrients (Fe, Mn, Cu, and Zn). However, significant increases in soil pH and electric conductivity in the soil were undesirable and could adversely impact plant growth. Application of such large quantities of ash also adds significant amounts of other elements that may be harmful to plants or to the environment. The use of such high land application rates in forest soils is strongly discouraged. Agronomic rates based on the ash liming capacity should be used instead.

CHAPTER 4
IMPACT OF HIGH-VOLUME WOOD ASH AMENDMENT ON SOIL METAL LOADING AND GROUNDWATER POLLUTION

Introduction

The increased popularity of land application of both municipal and industrial wastes has increased the vulnerability of soils to pollution. The release of trace metals (As, Cd, Cr, Cu, Mn, Ni, Se, and Zn) from materials applied to soils (including wood ash) may also pose a serious risk of contamination of groundwater. This release and mobilization depends on a variety of factors such as soil, material composition, metal and climate. The nature of the waste, e.g. ash matrix (Ferrailo et al., 1990), soil physical properties (Ghodrati et al., 1995) and distribution and frequency of rainfall (Khanna et al., 1994) play critical roles in the rate and extent of metal dissolution from the matrix. The physical and chemical properties of the soil and the speciation of the metal affect the mobility of the dissolved elements in the soil (Cullen and Reimer, 1989; Sparks, 1995). The vertical distance between the soil surface and groundwater levels governs the time the pollutants take to reach groundwater and the extent of dilution of pollutants before they reach groundwater.

Many State regulations on the use of non-hazardous industrial and municipal by-products use standards that were developed from sewage sludge studies (MDEP, 1989,

Sommers, 1977). However, sewage sludge has a very highly organic matrix compared to ash. The potential for pollution from ash may therefore be different from sludge, mainly because of the differences between solubility of metals in organic and inorganic matrices. Nonetheless, it is important to evaluate the acceptable application rates in relation to the same factors applied to sludge e.g. initial trace element content in soils, cumulative total load of metals, threshold values of trace metals and plant sensitivity.

A considerable number of studies on the solubility, distribution, and solubility-controlling solid phases of trace elements have been done on coal ash (Ainsworth and Rai, 1987), but very little has been done on the dissolution of trace metals from wood ash under field conditions. The main reason for this is that many of the studies on land application of wood ash used very low application rates and wood ashes in general have lower trace metal concentrations than most coal ashes.

Jardine et al. (1990) and Luxmore et al. (1990) concluded that ash applications of 44 Mg ha^{-1} or less on the moderately well-drained forest soils did not result in any deleterious effects on groundwater. This was not unusual because metals like Cd are strongly sorbed to Fe and Al oxides that are abundant in ultisols (Alloway, 1990) and their mobilities are inversely related to pH (El-Falaky et al., 1991). Iron (II) and organic matter in soil solution were also shown to affect the reduction of the more mobile and toxic Cr (VI) to Cr (III) which is less toxic and less mobile (Eary and Rai, 1991). Arsenic was sorbed by Fe and Al oxides (O'Neill, 1990) and hence arsenic mobility in these soils was limited. The authors note that it was very difficult to eliminate the effect of the different water table levels within and between the various treatments in their study.

Nonetheless, the ash application rate used in their study was relatively low (44 Mg ha^{-1} compared to up to 1800 Mg ha^{-1} in our study).

The behavior and fate of an organic or inorganic chemical added to soil depends on the manner in which it partitions itself among the dissolved, particulate and colloidal phases in the system. Geochemical reactions including ion exchange, complexation and speciation control the partitioning of solutes between the colloidal and aqueous phases. For example, highly charged cations or cationic species form very strong bonds with negatively charged colloidal surfaces. The fate of these species thus depends on the behavior of the colloids in that system (Buddemeier and Hunt, 1988). The role of colloids (both inorganic and organic) as carriers of metals in the subsurface has been demonstrated by many researchers (McCarthy and Zachara, 1989; Puls and Powell, 1992). The increase in the mobility of organics (caused by the increase in pH) and the presence of high concentrations of organic matter (mainly from ash, with little contribution from soil) make this channel of enhanced transport a potentially significant mechanism in our study. The increase in pH has also been shown to change the speciation of metals due to the low proton concentrations, thus significantly impacting the way they associate with colloids (Buddemeier and Hunt, 1988). The presence of large concentrations of salts (which impact ion exchange) from the ash used in our investigation provided us with a unique opportunity to study the influence of colloids under conditions of both high pH and salinity.

The objective of this study was therefore to determine the potential of metals released from ash to accumulate in soils and their potential to contaminate groundwater.

The second objective was to study the association of colloids with metals and the possible role colloids play in metal leaching to groundwater.

Materials and Methods

The site preparation and sampling for soil was carried out as described in Chapter 3. Each of the 15 plots monitored had two piezometric wells installed in it at the beginning of the monitoring study (after ash application). Each well was over six feet deep and protruded above ground level enough to prevent any standing water from seeping in and was capped. Groundwater was left to percolate into the well through the walls over a period of two weeks after which samples were collected using a pump. The sampling frequency was changed to once a month after 8 months. On the sampling day, the standing solution in the well was disposed of to allow "fresh" groundwater to collect. This fresh water was then pumped into polyvinyl chloride (PVC) containers slowly using an electric pump. Samples were transported in coolers (in ice) to the laboratory where they were immediately filtered through 0.45 μm filters upon arrival.

The concentrations of As, Cr, and Se in groundwater samples were determined using a Perkin Elmer SIMAA 6000 graphite furnace atomic absorption spectrophotometer. The spike recoveries for all elements analyzed were within 80 to 120% and the quality control samples were all within 10% of the known values. The pH and electrical conductivity were determined using an Accumet Model 20 pH / conductivity meter (Fisher Scientific) and the concentrations of Na and Ca were measured on the Perkin Elmer Varian 2380 graphite furnace atomic absorption spectrophotometer. The total organic carbon was

determined on the Shimadzu TOC 5050 total organic carbon analyser. The concentrations of Ca, Cd, Cl, Fe, Mn, Ni, and Zn were determined using a Thermo-Jerroll Ash 61E Inductively Coupled Plasma Atomic Emission Spectrophotometer (ICP-AES).

The extent of colloid facilitated transport was determined by filtering groundwater samples through two different size filters (1μm and 0.1μm). Samples for the colloid experiment were collected quarterly for a period of one year. The metal concentration in the solution that went through the smaller size filter (0.1μm) was considered to be the dissolved fraction while the concentration that went through the larger filter size was considered to be the sum of dissolved and colloidal fractions. The difference between these two was the metal concentration associated with colloids. Colloid characterization was done by filtering materials suspended in a solution that had been left standing overnight and collecting the residue for analyses with the X-ray diffractometer (Nicolet XRD Madison, WI) using CuKα radiation of aluminum powder mounts (Whitting and Allardice, 1986). The samples were also analyzed on a thermogravimetric analyzer (TGA, Omnitherm Corporation). All statistical analyses were carried out in SAS (The SAS Institute, 1982).

Results and Discussion

The fact that excessive amounts of ash were used in this study cannot be overemphasized. Most research on the impact of wood ash application on soil chemical and physical properties deals with much lower application rates (Mattigod et al., 1990; Naylor and Schmidt, 1989; Williams et al., 1996). Where large quantities of ash were

used (10 to 50% on a weight basis [Bilski and Alva, 1995; Ghodrati et al., 1995]), higher concentrations of trace metals were detected. The studies by Bilski and Alva (1995) and Ghodrati et al. (1995) used coal ash and not wood ash as was the case in our study.

Changes in Soil Metal Concentrations

Significant increases in Na concentrations ($p < 0.05$) in the treated soils were observed. Sodium concentrations increased from about 30mg kg^{-1} to 3000 mg kg^{-1} in the 1800 Mg ha^{-1} plots (Fig. 4-1a). The ash to soil Na ratio (650) was the highest of all metals analyzed and the over 400 times increase in Na concentration was a direct consequence of this. The excessive supply of Na was one of our biggest concerns in this study because Na disperses colloids and destroys soil structure leading to clogging and poor drainage, root penetration and trafficability (Brady and Weil, 1996). High sodicity, exchangeable sodium percent (ESP) greater than 15%, is undesirable because Na displaces plant essential nutrients from exchange sites leading to their increased leachability (Brady and Weil, 1996). The ESP was calculated as the exchangeable sodium divided by the CEC of the soil. Increased nutrient leaching leads to plant nutrient deficiencies.

Sodium concentrations decreased by 50% during the first four months (with a cumulative rainfall of about 500mm, Fig 4-1a) of leaching in the field indicating the high solubility of sodium salts. Sodium concentrations decreased to a maximum of about 160 mg kg^{-1} after two and half years of leaching signifying a decrease of almost 90% after 2500 mm of rainfall. Sodium salts leached out quickly from our ash amended plots as shown by the rapid decrease in concentrations from the upper levels of the profile

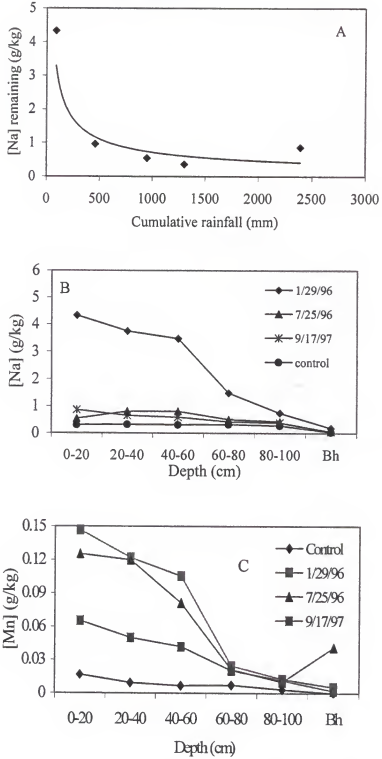


Figure 4-1.Surface [Fe] and [Mn] variation with rainfall (A) and depth (B, C) in the 1800 surface treatment

between the first and third sampling date (Fig. 4-1b). The Na concentration at the end of the study was nonetheless, five times the normal Na concentration of that soil. However, the decrease in hydraulic conductivity at our site was probably due to the fine nature of the ash particles rather than the contribution of Na to clogging. This sandy soil had very little structure and the added Na could not have significantly changed this structure. Instead, Na may have played a significant role in the rapid dispersion of organic matter in the soil.

Levels of Mn (Fig. 4-1c, 1800 Mg ha^{-1} treatment) and Fe (Table 2-2) were also significantly increased after ash application. Manganese concentrations increased from 0.02 to 0.06 and 0.15 g kg^{-1} representing an increase of 200 and 500% in the 900 and 1800 Mg ha^{-1} treatments respectively. Both increases were significant ($p < 0.05$) and significantly different ($p < 0.05$). Among the trace metals, Mn had the highest concentration in the ash and the highest relative concentration increase in the soil. This has also been shown to be true for ash from different sites (Naylor and Schmidt, 1986; Muse, 1993). Manganese plays a role in soil reduction/oxidation reactions because its higher oxidation state acts as a terminal electron acceptor in many biochemical reactions (Manahan, 1991). The concentrations of Mn in the ash-amended soils decreased to about 200% of the origin levels.

Surface Fe concentrations in the ash amended soils increased from a background concentration of 0.7mg kg^{-1} to 1.14 ($p > 0.05$) and 1.8 ($p > 0.05$) in the 900 and 1800Mg ha^{-1} treatments respectively (Table 2-2). Manganese and Fe are essential micronutrients for plant growth but they may become toxic to plants at high concentrations. Although the ash used in this study had very high concentrations of Mn and Fe (Table 2-2), both Fe and

Mn precipitate under conditions of high pH such as those used in this study. Iron and Al, and to a lesser extent, Mn, react with humic substances. When Fe and Al are present in large concentrations, this may lead to the precipitation of some of the organic matter that may be in solution at these high pHs. In our case, there was a very high concentration of DOC in solution thus increasing the Mn, Al and Fe carrying capacity of the soil solution. Hence, the mobility of Fe and Al in this soil may be explained by the greater DOC leaching, which would have precipitated with Al and Fe at low pH, under conditions of very high pH. Chapters 6 and 7 explore this topic further.

Table 4-1. Measured Fe and Al concentrations in soil during the first year of monitoring

Treatment	Fe (mg kg^{-1})				Al (mg kg^{-1})			
Depth (cm)	1/29/96	4/29/96	7/25/96	1/12/96	1/29/96	4/29/96	7/25/96	11/12/96
900 subsurface								
0-20	1.14±0.11	1.32±0.22	1.11±0.25	0.99±0.46	2.01±1.03	2.50±0.68	3.18±2.00	1.58±0.73
20-40	1.10±0.16	1.19±0.25	0.95±0.16	0.97±0.29	2.21±0.48	2.44±0.51	2.32±0.29	2.00±0.17
Bh	0.27±0.06	0.71±0.84	†----	0.18±0.05	0.77±0.94	1.89±0.92	----	0.92±0.40
1800 subsurface								
0-20	1.69±0.08	1.64±0.26	1.11±0.27	1.83±0.46	2.85±1.10	3.00±0.55	2.49±0.87	2.90±0.46
20-40	1.44±0.04	1.50±0.25	1.01±0.19	1.46±0.19	2.4±0.71	2.89±0.61	3.37±0.57	2.72±0.00
Bh	0.18±0.10	0.67±0.64	----	0.23±0.17	0.98±1.50	1.98±0.87	----	1.15±0.50
800 surface								
0-20	1.17±0.33	1.21±0.23	1.08±0.29	1.27±0.17	2.37±0.37	2.67±0.61	4.20±0.15	2.48±0.50
20-40	1.09±0.16	1.20±0.23	0.98±0.17	1.23±0.21	2.35±0.84	2.54±0.87	4.54±0.40	2.46±0.12
Bh	0.17±0.14	0.19±0.15	----	0.21±0.16	1.10±1.31	2.34±1.00	----	0.52±0.40
1800 surface								
0-20	1.86±0.27	1.69±0.26	1.60±0.23	1.48±0.22	2.88±0.78	2.89±3.84	4.3±0.68	2.46±0.65
20-40	1.56±0.45	1.74±0.29	1.50±0.29	1.60±0.31	2.61±1.21	3.02±0.44	3.20±0.64	2.62±0.35
Bh	0.17±0.10	0.12±0.01	----	0.36±0.30	0.94±0.57	0.90±0.76	----	1.11±0.17
Control								
0-20	0.66±0.10	0.98±0.35	0.74±0.08	0.51±0.34	1.65±1.78	2.06±1.62	4.8±0.57	1.26±0.45
20-40	0.72±0.06	0.78±0.02	0.70±0.04	0.72±0.10	1.88±1.76	2.28±0.15	4.30±0.25	1.88±0.25
Bh	0.10±0.08	0.14±0.05	----	0.16±0.06	0.80±2.04	0.71±0.31	----	0.69±0.21

† Soil at Bh horizon was too wet to collect

The increase in soil Al concentration was small (from 1.8 mg kg^{-1} to 2.0 ($p > 0.05$) and 2.8 ($p < 0.05$) for the 900 and 1800 Mg ha^{-1} treatments respectively, Table 4-1)

compared to the input from the ash. Concentrations of exchangeable Al were even lower (data not shown). This may have been due to the precipitation as Al-hydroxides or Al-organic matter complexes and gibbsite formation at the pHs involved. A high Al/Ca ratio in soil solution increases the likelihood of Al saturation of surface adsorption sites on roots (Godbold et al., 1988; Cronan, 1991) and this may reduce Ca and Mg uptake and lead to nutrient imbalances. Aluminum toxicity also increases root mortality and turnover in many crops and plants (Rengel, 1992).

Although concentrations of Zn, Cu, Cd, Pb and Ni were significantly increased ($p < 0.05$) from ash application, their increases were not high enough to warrant further investigation for this part of this study (data not shown).

Arsenic, Cr, and Se concentrations all initially increased significantly ($p < 0.05$) after ash application. Arsenic concentrations increased from background values of 0.3 to < 2 mg kg^{-1} but they decreased to 0.27 to 0.60 mg kg^{-1} with time (Fig 4-2a). The decrease in the concentrations of these elements was not as rapid as that of the major cations, Na, Ca, Mg and K. Chromium concentrations reached a maximum of < 5 mg kg^{-1} before decreasing to background levels (Fig 4-2b). The increase in Se levels was relatively lower than the other two elements taking into account its high ash to soil concentration ratio (Table 2-2, Fig 4-2c). The ratios of concentrations of As, Cr and Se in the ash to soil were all low (5, 0.5 and 19 respectively). This explains the low accumulation of these three elements in the treated soils. Arsenic, Cr and Se move in the soil as anions and are therefore not easily retained by the mostly negatively charged colloid surfaces (clay and organic matter) if they are present in significantly large concentrations. In our case, these elements were present at low levels and therefore other soil factors may have taken

precedence over their mere charge. For example, the negatively charged arsenate, chromate and selenate species can associate with positively charged surfaces in humic substances through electrostatic attraction thus enhancing the leachability of these oxyanions.

Trace metal mobility seemed to be affected more by soil properties than the major cations (Ca, Mg, K and Na) discussed in Chapter 3. This was possibly due to their presence in relatively lower concentrations. The Bh horizon temporarily retained some of the leached metals but these were eventually leached out when the organic colloids in this horizon were extracted by the alkaline leachate (Fig. 4-2). Significant portions of the trace elements had been leached out by the end of the first summer after incorporation (Fig. 4-2a,b,c). The CEC of our soil was very low (~ 4 cmol kg^{-1}), but even if this was high, its effect on these oxyanions would have been insignificant because of their charge. The organic matter content of this soil was also very low (< 1%) and although this amount may have been sufficient to hold significant proportions of trace metals, the high pH induced by the ash actually changed this beneficial aspect into a potential carrier of metals to groundwater.

Groundwater Analyses

Groundwater collected from both application rates was dark colored (from light to very dark brown) indicating the presence of large quantities of organic matter. Samples from the 1800 Mg ha^{-1} treatments had a darker color (almost coffee colored) due to DOC (Fig. 4-3a). The high pH associated with the alkaline constituents of the ash was

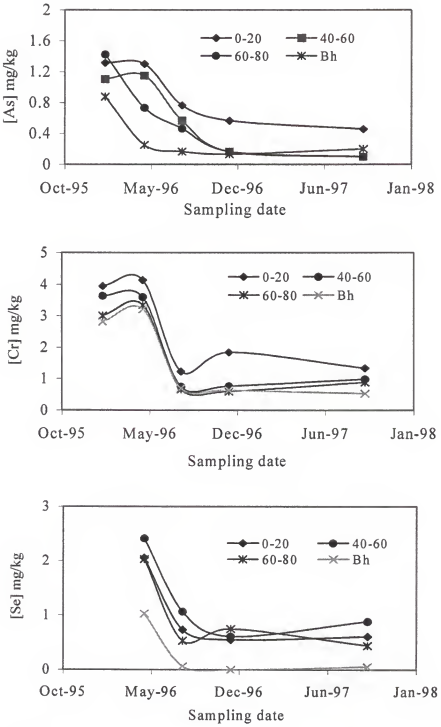


Figure 4-2. Changes in concentrations of As, Cr and Se at different depths in the 1800 surface treatment. The variation for the other rates and application methods (Appendix) showed the same pattern with the subsurface method showing higher initial concentrations.

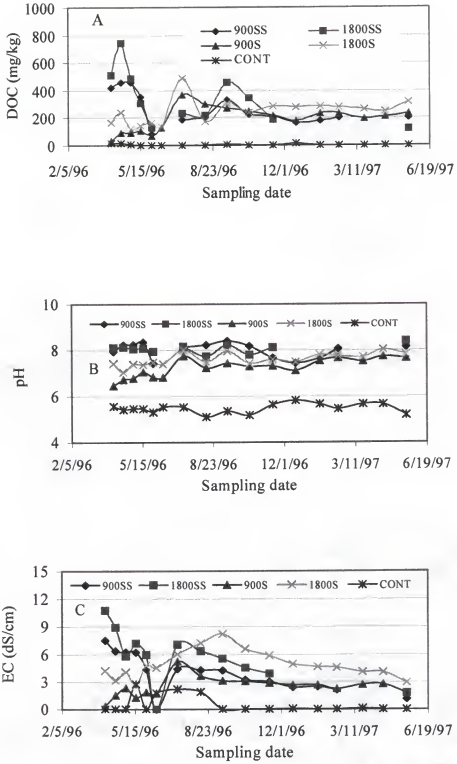


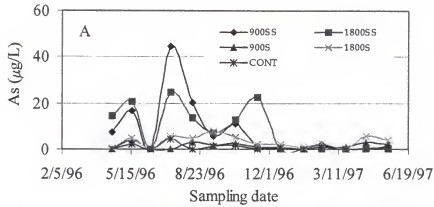
Figure 4-3.Variation for each application rate and method with time (a) DOC, (b) pH, and (c) EC

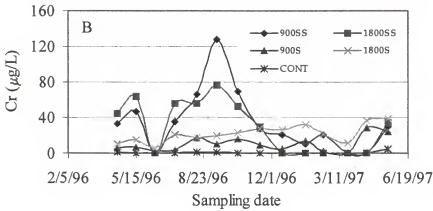
SS – subsurface ash application and S - surface ash application

responsible for the dissolution of the organic C from both the surface and spodic (Bh) horizons in the higher treatments. The Bh horizons in the subsurface treatments had more bleaching because the alkaline leachate in these plots traveled shorter distances (50 cm lesser) to reach the Bh horizon and hence there was very little dilution. The DOC leached from these profiles (Fig. 4-3a) support this observation. The nearly immediate change in groundwater pH, EC, and DOC showed that the salts were very soluble and leached out rapidly.

Most studies on the environmental impact of ash application do not even consider changes in groundwater pH because the low application rates used in those studies do not warrant it. In our study, groundwater pH increased from 5.5 to above 7 for both the 900 and 1800 Mg ha^{-1} surface treatments (Fig. 4-3b). The increase in groundwater pH in the subsurface treatments was numerically higher but not statistically significant ($p > 0.05$, pH rose to 8 in both application rates) than that in the surface treatments. The increase in pH was due to the dissolution and subsequent hydration of the alkali and alkaline earth metals (Na, K, Ca and Mg) in the ash (Manahan, 1991). The higher increase in the subsurface treatments was a result of the shorter distance (47cm shorter) that the dissolved salts had to travel in the subsurface treatments. This reduces the number of potentially adsorbing sites for the cations in solution. Consequently, more salts from the subsurface horizons reached the groundwater. The decrease in salt concentration (signified by reduction in EC) with time was possibly due to dilution as more rainfall fell or settling to deeper layers beneath our sampling depth.

It took about half a year before increases in As, Cr and Se were detected in the groundwater. This was in agreement with our postulation that trace metals interact more





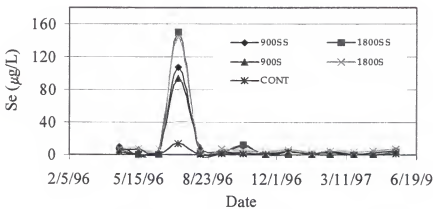


Figure 4-4. Changes in groundwater (a) As, (b) Cr, and (c) Se for each application rate and method with time

with the soil matrix than the other cations. This was in spite of the high pH conditions that reduce the oxyanion adsorption due to a decrease in positively charged soil exchange sites (favoring oxyanion leaching, Kahl et al., 1996). Concentrations of most trace metals in groundwater showed increases after 6 months, but they decreased with time. Concentrations of all the metals monitored were however, below the National Primary Drinking Water Standards (NPDWS) set by the USEPA at the end of the monitoring study.

Arsenic concentration increased to about 48 µg/L (below NPDWS value of 50 µg/L) but it decreased to less than 5 µg/L in the subsequent six months (Fig. 4-4a). Arsenic concentrations in the ash were not high enough (five times higher those in soil; Table 2-2) to significantly increase concentrations in groundwater above the NPDWS values even at the high application rates used. It is important to keep groundwater As levels low because it is a carcinogen, teratogen and mutagen. Arsenic replaces P in deoxyribonucleic acid (DNA) causing mutations.

Chromium concentrations increased to just below 130 µg/L and decreased in a similar fashion to As. This was however a cause for concern since Cr stayed above the regulated value of 50 µg/L for a few months. Chromium levels in groundwater should be kept low because the presence of many other sources of Cr in the environment e.g. Cr plated metals, paints and CCA (chromium, copper and arsenic) treated wood make its concentration prone to rapid fluctuations. Chromium is a known carcinogen and possible teratogen.

The increase in Se was much sharper (concentrations increased to about 155µg/L) and dropped down to their initial concentrations steeply after only three months. The

sharp increase in Se concentrations in groundwater was expected as it was the least retained by the soil matrix (Se concentration in soil was not as high as expected, given its abundance in ash). Cadmium concentrations (not shown) rose above the regulated value of 5 μg/L (Cd concentration peaked at 12 μg/L) for three months after the initial six months. Although the ash to soil Cd concentration ratio was 6, Cd solubility was lower than the other elements studied. The increase in total Cd concentrations to above the NPDWS values is nonetheless a cause for concern because it is a carcinogen (Manahan, 1991).

The application rates used in this study were high enough to elevate groundwater levels of trace metals (As, Cr, Cd and Se) above the NPDWS values. These rates need to be lowered not only to comply with state and federal regulations, but to save groundwater from the avalanche of DOC and other salts observed in this study. This ensures the continuous survival of life forms that carry out the vital nutrient recycling and water purification processes in groundwater.

Contribution of Colloids

Analyses of groundwater samples from a Nevada nuclear test site showed that Mn, Co, Sb, Ce and Eu were associated with colloidal size particles (Buddemeier and Hunt, 1988). Analyses of physically separated groundwater samples in our study indicated that Cu, Cr and As were associated with colloids ($p < 0.05$). The extent of colloidal association was highest in As, with As-colloid associations constituting 40 to 55% of the total As in groundwater from the 900 and 1800 Mg ha^{-1} treatments

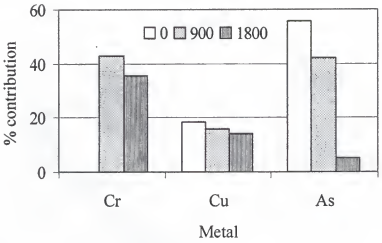


Figure 4-5. Comparison of extent of colloidal transport in metals

respectively (Fig 4-5). However, it must be noted that the concentration of As was very low, leading to any small changes in colloid associated As having a big impact on the overall percentage contribution of colloids. Chromium had the second highest association with colloids (42 and 35% for the 1800 and 900 Mg ha^{-1} treatments respectively). Chromium (VI) has been shown to react with some high molecular weight humic substances and this may have contributed to these high percentages of associations. Copper, whose association with organic colloids has been documented extensively, was not as affected by colloids as expected (only about 20% of Cu in groundwater was associated with colloids in both treatments). The answer to this puzzle may lie in the vast differences between the chemical conditions in this study and those used by other researchers. The pH and electric conductivity of the soil at our research site after ash application was very high and this had significant implications in the speciation and subsequent reactions of Cu in our system. As explained in Chapters 7 and 8, the high EC

associated with our ash may have led to some organic molecules precipitating out of solution, taking a significant amount of Cu out of the liquid phase.

Our method of separation of the two fractions (colloidal and non-colloidal) may also not have been rigorous enough to separate the truly dissolved from the colloidal material. There were many artifacts that may have affected our results including filter paper flaws, the operationally defined boundary between colloidal and non-colloidal metals of 0.1 μm and changes during sampling and transportation of samples.

The colloids in the groundwater in this study were mostly organic macromolecules dissolved from both the ash and the topsoil, and clay sized quartz and small amounts of kaolinite (Fig. 4-6). Organic colloids constituted more than 60% (w/w) of the colloids in groundwater. There were >1% gibbsite, gypsum and kaolinite, and >10% quartz in the inorganic colloids from groundwater. Another source of error in our study came from the association of some of the metals with calcite and lower molecular weight organic compounds in the soil that could not be separated from the dissolved fraction using our operationally defined boundary. Calcite was not accounted for in our analyses as most of it was in solution at the pH conditions involved and was actually included with the dissolved fraction. The contribution from Mn and Fe oxides may also have been significant but they went undetected because X-ray diffraction will only detect components that constitute > 1% of the sample. For example, it has been reported that over 90% of Cd and As present in a column of sand were found to be associated with Fe and Mn (Puls and Powell, 1992).

The results from the colloid study were not very conclusive. There is a definite

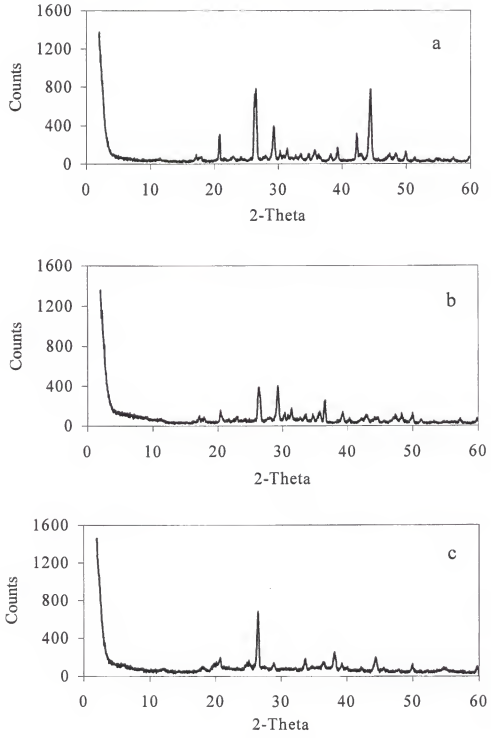


Fig 4-6. X-ray diffraction curves for (a) ash on Al mount, (b), ash on plexiglass mount and (c) dried colloidal material from groundwater

need for further study of our colloidal material with scanning and transmission electron microscopy (SEM and TEM) in order to identify the specific metal-colloid interactions. Specific column studies also need to be conducted to verify whether the associations we found in groundwater were a result of reactions that happened at groundwater level or the metals were transported in association with colloids from the top profiles. There is also need for a thorough characterization of the organic colloid fraction to further understand their interaction with our metals under the conditions of this experiment.

Conclusions

Results from this study showed that high pH and electrical conductivities in the treated soils were high enough to pose negative effects on plant growth. In terms of application method, the subsurface application method was not only cumbersome and costly, but had no advantage over the surface treatment in terms of environmental impact. In fact, there was a shorter distance for the leachate to travel to the water table in the subsurface treatments leading to significantly higher groundwater contamination than surface application.

There are multitudes of factors that change forest nutrient dynamics. The results presented in this chapter depend on the solution composition, pH dependent soil chemical equilibria, and other factors which affect the hydraulic properties of our specific soil. Results obtained from this study may therefore not apply under different conditions until a full characterization of the properties of trace metals under those conditions is done.

Nonetheless, the application rates used in this study were too high for this site given the sandy nature of the soil matrix and the high rainfall the area gets. For compliance with both State and Federal regulations, much lower rates should be used.

CHAPTER 5
EFFECTS OF ACIDIFICATION ON METAL MOBILITY IN A BOILER ASH AMENDED SOIL

Introduction

The adverse effects of wood ash on groundwater are not well known. Previous research on trace metal contamination of soils mainly focused on sewage-sludge amended soils. The few studies done using wood ash generally employ very low application rates. Compared to our study, the potential for soil metal loading and groundwater contamination is very low in those studies.

Wood ash consists of salts, oxides and hydroxides of Ca, Mg, Na, and K (Hakkila, 1986; Lerner and Utzinger, 1986) and low amounts of the trace metals including As, Cd, Cr, Cu, Mn, Ni, Se and Zn (Etiegni et al., 1991; McGinnis, 1995; Pepin and Coleman, 1984; Unger and Fernandes, 1990; Williams et al., 1995), with an average pH of 12.4 (Someshwar, 1996). Other elements present include N, S, Al, Fe, Si, Ba and Mo. Generally, wood ash is low in toxic trace metals but most of these are readily soluble because the solid matrix is mainly composed of salts (Unger and Fernandes, 1990; Muse and Mitchell, 1995). Ash also has a very high pH (up to 13) and this tends to affect not only the solubility of metals from the ash matrix, but their subsequent leachability and reaction with soil constituents. The high pH induced by ash leads to precipitation of micronutrients becoming unavailable for plant uptake and high salinity increases osmotic

pressure and this has significant implications for plant water uptake and ultimately, growth.

The metals that are introduced with ash application may end up held onto exchange sites of organic/inorganic solids, occluded in, or fixed onto soil minerals, taken up by the biological component (Mattigod et al., 1990) or in our case, dissolved in soil solution or precipitated with other compounds. Understanding the processes governing the accumulation, migration and plant availability of chemical elements like As, Cd, Cr, Cu, Se and Zn in the soil is, hence, essential for predicting the environmental impact of spreading wood ash on land.

The main impact from land application of wood ash is elevated soil pH, which can adversely affect tree growth. Higher pH also leads to solubilization of organic matter and has a negative impact on soil biota. DOC complexes with metals (Buffle, 1988; Lafrance et al., 1989; Sauve et al., 1997) from ash and increases their mobility especially under conditions of high ionic strength (Boyle and Fuller, 1987). Solubilization of organic matter also removes a sink of metals in the soil and mobilizes colloids that may enhance metal transport. Reducing soil pH to a more acceptable level for tree growth and reduction in organic matter solubilization via acidification is a possible solution. However, the effects of acidification on metal mobility in ash amended soils need to be evaluated in the laboratory before such a practice is used in the field. The pH was reduced to 6 and 7 because lower pHs have been shown to increase the availability of trace metals in solution and this increases their chances of being leached to the groundwater.

The primary objectives of this investigation were to determine: 1) the effect of acidification (to pH 6 and 7) on the leachability of As, Cd, Cr, Cu, Ni, and Se from a sandy forest soil amended with high-volume (900 and 1800 Mg ha^{-1}) of boiler ash; 2) the effect of age of ash on trace metal leachability, and 3) the effect of leaching frequency on metal leachability. This study complements an on-going field monitoring study, in which the same ash was applied to a soil at 900 and 1800 Mg ha^{-1} in December of 1995. Hence, the results obtained from this study will be useful for the on-going, as well as future directions for, land application of wood ash.

Materials and Methods

Soil and Ash Collection

The soil samples used for this study were collected in April 1997 from a research site in Hawthorne, Florida (Fig. 3-1). The soil is an acidic fine sand (typic quartzipsamment) with a spodic horizon below 2 m. The soils were mixed to ensure homogeneity, air-dried and sieved through a 1 mm sieve. Two types of ash (fresh ash and aged ash-about one and half years old) were tested. For the leaching study using aged-ash, representative samples were collected from research plots to which 0, 900 and 1800 Mg ha^{-1} of boiler ash were applied at the surface and incorporated to a depth of 47 cm in December 1995. Three soil samples representative of the A (47 cm including ash), the elluvial E (150cm), and spodic horizons Bh (20 cm), were collected from each treatment and packed in columns in proportion to their actual soil depth in the order of A-E-B. For the leaching study using the fresh ash, soil samples were collected from the control plot (to which no ash was added) and ash was mixed with surface soil (A horizon) to a depth proportional to the field value of 47

cm at rates equivalent to 900 and 1800 Mg ha^{-1}. The fresh ash-soil samples were then packed in the same order as the aged-ash leaching columns (to the same bulk density). Some of the chemical properties of the ash and soil are presented in Table 2-2.

The main difference between aged and fresh ash was that aged ash had been incorporated into soil in the field and leached for one and half years, and fresh ash was taken from the end of the production line at the plant. The fresh ash therefore had higher salinity and higher pH (pH > 11 before incorporation into soil and pH 10 after mixing with soil) than the aged ash (pH 9 after mixing with soil) because it had not been preleached. The aged ash-soil columns also had lower DOC concentrations due to leaching in the field.

Experimental Treatments

Two column leaching studies were conducted to determine the effects of acidification and time on metal mobility in an ash-amended forest soil using two types of samples: aged and fresh ash. The columns used were 12.8 cm long x 2.75 cm (diameter) and the soil was packed to about 11 cm depth. The total weight of soil and ash (2.65 and 5.30 g for the two rates) in each column was 80 g giving an approximate bulk density of 1250 kg m^{-3}. Each treatment was duplicated.

Aged Ash Columns

Aged ash-soil profiles were collected from the field, where the ash-soil profile was exposed to approximately 1700 mm of rainfall for about one and half years before sampling. The results of this study will be useful to determine if acidification of the

current field is feasible to reduce groundwater contamination. The corresponding design was an unbalanced 3 (ash level) x 3 (pH) x 2 (sampling period) randomized block design. This design was adopted because the control (0 ash) treatment did not have different levels of acidification.

The ash-soil profile pH was adjusted from an initial value of ~9 to 7 and 6 using dilute HNO_3. The amounts of HNO_3 required to reach target pHs were determined by acid titration of a mixture of ash and soil in the proportions that were to be used in the experiment. A titration curve was developed for each treatment. To ensure uniformity and accuracy, an ash paste was titrated with dilute HNO_3 and left to stand for three days and titrated again to the target pH. The predetermined amount of HNO_3 was mixed with water to bring the column to field capacity and applied to the column in one dose immediately after packing and left to stand until the first leaching. Slight differences between the target pH and actual pH attained were attributed to the heterogeneity of the ash samples.

Fresh Ash Columns

A freshly prepared ash-soil profile, where ash was mixed with surface soil (from the control plots) was packed in a column in the laboratory to the same depth and at the same rate as the field experiment (900 and 1800 Mg ha^{-1}). The results of this study will be useful to determine if acidification should be done before or with land application of wood ash. The ash-soil profile pH was adjusted from the initial value of ~10 to 7 and 6 using dilute HNO_3 using titration curves as was done for the aged ash columns.

One set of ash-soil columns from both the aged and fresh profiles (comprising of both rates, duplicated) was left unacidified while the other two sets were acidified to pHs

of 6 and 7. The leachate pHs were within 0.3 units of the target pHs. Leaching was carried out with 50 mL of double deionized water over a period of 24 hours using a simple laboratory extractor (Zero-Max extractor model 24-01, Nebraska, USA) under pyrostatic pressure. The extractor used mechanically operated syringes connected to 60 mL syringe extraction barrels. The reservoir barrels were mounted on top of the extraction barrels with tight fitting rubber sleeves which coupled the leaching flow rate to the rate of the plunger withdrawal. One set of soil columns was leached 7 days after incubation at field capacity and another set after 35 d to evaluate the effects of reaction time on metal leachability. For the second leaching study using the fresh-ash, the same soil columns were leached after 7 and 35 d (sequentially) to determine continued leaching on metal leachability. The design of our leaching experiments allowed constant and fast mass flow of leaching solution through the column such that products of dissolution were continuously removed from the column. The data were analyzed for Analysis of Variance using the Statistical Analyses System (SAS, 1982).

Chemical Analyses

Leachates were filtered through a 0.22 μm membrane filter under pyrostatic pressure immediately after each leaching event and stored in a refrigerator prior to analysis. Concentrations of As, Cd, Cr, Cu, Ni and Se were determined using a Perkin-Elmer SIMAA 6000 Atomic Absorption Spectrophotometer. The spike recoveries for all six elements were within 100±20%, and the quality control samples were all within 100±10% of the known values. Nickel analyses showed matrix interference but not enough to warrant the use of standard addition method. The leachate pH was determined using an Accumet

Model 20 pH / conductivity meter (Fisher Scientific). Concentrations of Na and Ca were measured using a Perkin-Elmer 2380 Atomic Absorption Spectrophotometer. The DOC in the leachates was determined using a Shimadzu TOC 5050 Analyser.

Results and Discussion

The pH of the fresh ash-soil profile (pH=10) was greater than that of the aged ash-soil profile (pH=9, Figs. 5-1 and 5-2). Apparently, most of the differences in chemical properties between these two samples stemmed from the one and half years of natural leaching of calcium carbonate and other salts from the aged ash. Soil pH was reduced by one unit, and DOC and electrical conductivity by a factor of 10.

Leaching of the Aged Ash-soil Profile

Studies have shown that total metal concentrations in the solid matrix are poor indicators for metal leachability in soils (Adriano, 1986; Pohlman and McColl, 1986; Ma and Rao, 1997). Similarly, total metal concentrations in wood ash correlated poorly with metal leachability. Concentrations of Cu, Cr and As in the ash were 37, 2, and 2 mg kg^{-1} (Table 2-2), respectively, whereas they were 7.5, 10.8, and 18.0 $\mu g\ g^{-1}$, respectively, in the leachates of the unacidified 1800 Mg ha^{-1} treatment after 7 d reaction (Figs. 5-1 and 5-2). Total Cu concentration was the highest among the three metals in the ash, but Cu mobility was the lowest in the leachates. Smith et al. (1995) reported that the metal

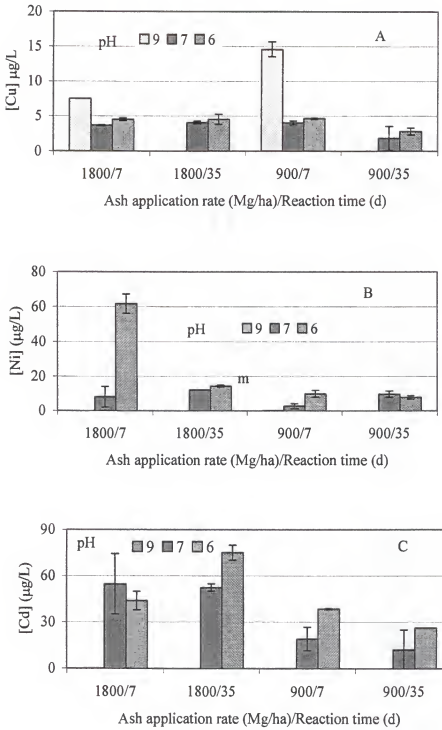
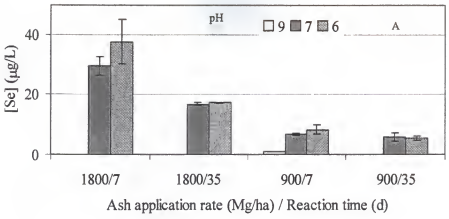
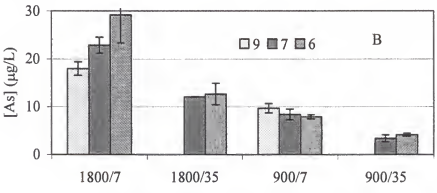


Figure 5-1. Changes in leachate concentrations of (a) Cu, (b) Ni, and (c) Cd with reaction time in the aged ash-soil columns. The samples were leached at different intervals from the beginning of the experiment. The rates used were on a weight to weight basis.





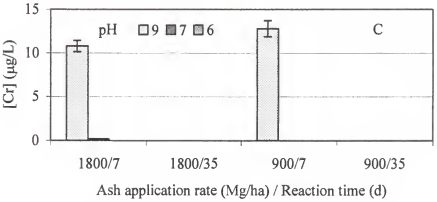


Figure 5-2. Changes in concentrations of (a) Se, (b) As, and (c) Cr with reaction time in the aged ash-soil columns.

mobility sequence in 10 soil types (across six orders ranging from sands to clays with pHs varying from 4.2 to 7.8) was Cu < Cd < Ni for cations and Se < As < Cr for oxyanions. The metals were not all leached to the same extent (clays showed higher attenuation capacity than sands), but the order of leaching was generally the same. The soil type of Smith et al. (1995) that most resembled the one used in this study (a spodosol) showed moderate mobility of metals due to the presence of a spodic horizon. However, that soil was not impacted by high pH and salinity as was the present case.

The concentrations of As, Cu, and Cr in the leachates decreased significantly ($p < 0.05$) as incubation time increased from 7 to 35 d for the 900 and 1800 Mg ha^{-1} unacidified treatments (Fig. 5-1a,b). Similar results were obtained for Pb in a soil column study by Ma et al. (1995). It was unclear what was responsible for the significant metal reduction in these ash-soil columns. In a study of transformation of added trace metals in soils under saturated conditions, Misra et al. (1990) also reported significant decline in concentrations of DTPA extractable Zn, Cu, Ni, Cd, Pb and Cr as incubation time increased from 0 to 120 d. Precipitation as sulfides and carbonates, and fixation by clays, organic matter and Fe/Mn hydrous oxides were proposed as possible mechanisms, but no definitive evidence was provided (Misra et al., 1990). Little Cd, Ni, or Se was detected in the leachates in the unacidified treatments (Figs. 5-1 and 5-2) although their total concentrations in the wood ash were relatively high, i.e. 3, 10 and 19 mg kg^{-1}, respectively (Table 2-2). Perhaps most of these metals had already been leached out in the field.

There was a striking difference in the color of leachates between the acidified (leachate pHs ~6 and ~7) and unacidified (leachate pHs 9-10) ash-soil columns. Leachate

colors from the unacidified columns ranged from light yellowish brown to coffee colored in contrast to clear leachates from the acidified columns. The high pH associated with alkaline salts in the unacidified treatments was presumably responsible for dissolution of humic substances from the ash-soil columns, and the spectrum of colors observed. These observations were supported by the DOC concentrations in these samples (Table 5-1 except for 900/9-10 in the aged ash). Concentrations of DOC significantly decreased as a result of acidification, possibly due to precipitation of humic acids which were responsible for the dark colors in the leachates of unacidified profiles (pH > 9).

Table 5-1. Concentrations of Na, Ca and DOC in leachates from two leaching studies after 7 d of reaction (mg kg^{-1}).

Ash rate/	Aged ash-soil profile			Fresh ash-soil profile		
Target pH	**Na**	**Ca**	**DOC**	**Na**	**Ca**	**DOC**
900/9-10[†]	440±98.0	18.0±4.80	3.70±1.1	4160±98.0	24.0±0.00	434±49.0
900/7	922±0.00	340±100	4.60±0.5	4840±290	998±2.70	23.4±0.50
900/6	990±98.0	470±0.00	3.90±0.6	3810±195	476±53.0	12.9±0.80
1800/9-10	920±0.00	0.84±1.00	27.0±6.1	5460±270	188±205	525±71.0
1800/7	2230±875	1050±260	3.70±0.1	8220±390	764±7.90	32.6±7.00
1800/6	1470±0.00	960±60.0	2.80±0.1	8700±98.0	2820±330	66.1±0.70

[†] Aged soil-ash profiles had an original pH of 9 whereas the fresh soil-ash profiles had a pH of 10. After acidification the pH were 6 or 7. There were only minor deviations (± 0.2 pH units) from these target values. All values are reported as mean ± standard deviation between replicates.

Concentrations of Cd, Ni, Se and As increased significantly ($p < 0.05$) in the leachates of all acidified treatments; generally, greater acidification resulting in greater metal concentrations (Figs. 5-1 and 5-2). The acidified 900 Mg ha^{-1} treatments had significantly lower concentrations of Cd, Ni, Se and As in leachates than the acidified

1800 Mg ha^{-1}, and there was no bleaching of the organic layer (Bh); both observations can be attributed to lower ash loading.

Three possible mechanisms may explain increased mobility of Cd, Ni, Se and As upon acidification. Reduced soil cation exchange capacity (Brady and Weil, 1996; Sparks, 1995) and increased Na concentrations upon acidification (Table 5-1) may enhance Cd and Ni mobility in acidified ash-soil columns. The CEC of the soil used in this study was very low (4 cmol kg^{-1}) and so this effect may be minimal. Calcium carbonate, whose presence was confirmed by x-ray diffraction, constituted ~20% of the boiler ash (Table 2-2). These metals were possibly adsorbed on the $CaCO_3$ surface during the one and a half years of natural weathering in the field (McBride, 1980) or co-precipitated with calcium carbonate during the combustion process (Someshwar, 1996). Upon acidification, Ca concentrations in the 900 Mg ha^{-1} treatments increased from 18.1 to 343 to 470 mg kg^{-1} possibly from $CaCO_3$ dissolution (Table 5-1). As a result, Cd, Ni, Se and As adsorbed on the $CaCO_3$ were released. On the other hand, concentrations of Cu (Fig. 5-1) and Cr (Fig. 5-2) decreased significantly upon acidification after 7 d of incubation. Reduced Cu concentrations may be related to strong Cu complexation with humic substances (Bloom, 1981). Under alkaline conditions (pH=9), most Cu in solution was probably associated with dissolved humic acids, and was relatively mobile. Upon acidification, soluble Cu-humic complexes may precipitate, reducing Cu mobility. This hypothesis was supported by reduced DOC concentrations upon acidification (Table 5-1).

Reduced Cr mobility may result from reduced Cr solubility upon acidification (Eary et al., 1990). Chromium leachability is closely linked to its oxidation state (Bartlett and Kimble, 1976a,b). The presence of high Mn concentrations in our ash may have

maintained Cr in the reduced state as is the case in many ashes (Someshwar, 1996). More Cr (III) is adsorbed with an increase in pH whereas Cr (VI) is minimally adsorbed at 8.5. Chromium (III) also forms stable complexes with the carboxyl groups on humic acid, further limiting its solubility (Manahan, 1991). At relatively low pH, Cr (III) is significantly hydrolyzed to $Cr(OH)^{2+}$, $Cr_2(OH)_4^{2+}$, or $Cr_6(OH)_{12}^{6+}$, which are adsorbed through cation exchange (Eary et al., 1990). The chromate species responsible for the increase in total chromium in this study may hence be Cr (III).

Leaching of the Fresh Ash-soil Profile

Metal leachability in the unacidified fresh ash-soil profile was in the increasing order of Cd < Ni < Cu and Se < As < Cr (Table 5-2), which was in general agreement with the order of Cu < Cd <Ni and Se < As < Cr reported by Smith et al., (1995), except for Cu which was very mobile in our columns (Fig. 5-3). Mobility of Cu increased from the lowest to the second highest among the six metals, whereas that of Ni was greater than that of Se in our system (Table 5-2). Our soil was impacted by high rates of boiler ash, which resulted in an elevated pH of 10 (in columns) compared to a normal soil pH of 5.6. High alkalinity from the ash dissolved humic substances in the soil, leading to high DOC in the leachates (Table 5-2). High DOC may explain greater Cu and Ni leachability in this soil than in normal soils (Bloom, 1981).

Metal leachability in the fresh ash-soil profile was generally 9-15 times greater than that in the aged ash-soil profile except As, which was 3 times greater (Figs. 5-1 and 5-2). Sodium concentrations in the 900 Mg ha^{-1} treatment after 7 d of reaction in the fresh ash-soil profile were ten times those in the aged ash-soil profile (Table 5-1).

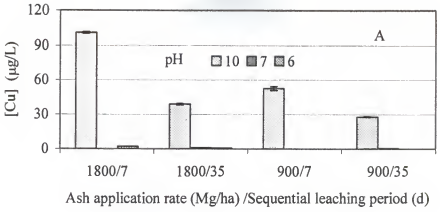
Table 5-2. Comparison of metal leachability in this study to that of Smith et al., (1995).

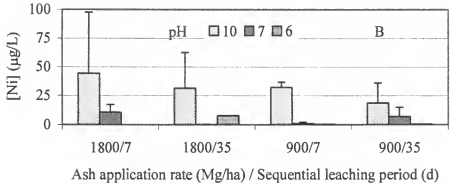
Order of	Unacidified		Acidified to pH 7		Acidified to pH 6	
Leachability	Aged	Fresh	Aged	Fresh	Aged	Fresh
Smith et al., (1995)[†]	Metal concentration ($\mu g\ L^{-1}$) in current study					
Cu (1)	7.5	101	3.7	0	4.55	2.1
Cd (2)	0.15	1.3	54.8	3.55	44.0	1.1
Ni (3)	0.0	44.3	8.2	10.6	61.7	0.0
Se (1)	0.0	21.4	29.6	18.3	37.8	4.6
As (2)	18.0	60.2	22.9	0.0	29.2	3.2
Cr (3)	10.8	161	0.2	76.2	0.0	8.6

[†] The number in parenthesis represents the leaching sequence observed by Smith et al., 1995 among three cationic metals and three oxyanions.

Interestingly, sodium leaching was not faster than other metals in the soil even though its leachability is significantly greater than most metals, possibly due to its extremely high concentrations (26 $g\ L^{-1}$).

Unlike the aged ash-soil profile, acidification of the fresh ash-soil profile significantly reduced the leachability of all metals. Greater acidification generally resulted in greater reduction in metal leachability (Figs. 5-3 and 5-4). In terms of relative metal concentration reduction upon acidification, Cu and As had the greatest concentration decrease followed by Ni, Cr, Se and Cd (Cd was inconsistent) (Figs. 5-3 and 5-4), which can be partially attributed to reduction in DOC concentrations upon acidification (8 to 33 fold, Table 5-1). In their investigation of the nature and transformations of Se, Zawislanski and Zavarin (1996) noted that soils with high organic carbon had high levels of organically associated Se. The stabilized spodic horizon in the acidified treatments may explain why there was less Se in the leachates from these treatments. Selenate adsorption increased with decreasing pH because the effectiveness of ligand exchange





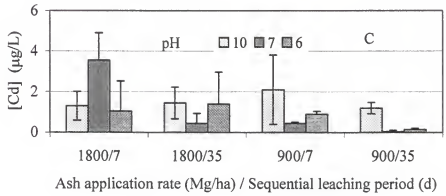
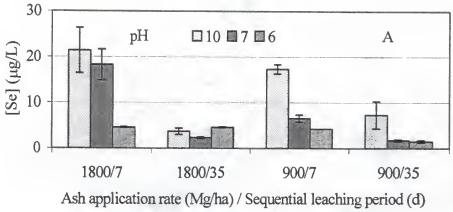
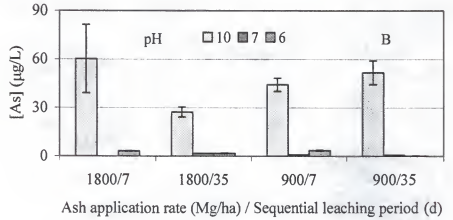


Figure 5-3. Changes in concentrations of (a) Cu, (b) Ni and, (c) Cd with leaching period in the fresh ash-soil columns. These columns were leached sequentially, unlike the first study.





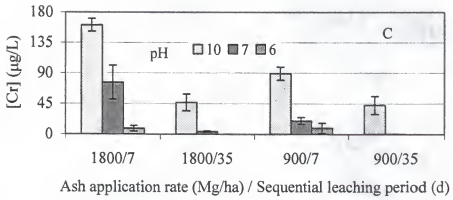


Figure 5-4. Changes in concentrations of (a) Se, (b) As, and (c) Cr with leaching period in the fresh ash-soil columns.

increases with increasing H^+ concentration. Cary et al. (1977b) found that downward movement of Cr (VI) in soil columns was greater in alkaline soils than in acid soils indicating that this species was not easily sorbed at high pH. The formation of polynuclear complexes that can be adsorbed by soil components improves chromate adsorption as opposed to monomeric forms like K_2CrO_4. The higher ionic strength in the leachate also depresses the diffuse double layer surrounding clay particles, allowing more adsorption from the leachate solution. The fact that reduction in Cu concentrations was the greatest and Cu complexation with organic acids the strongest among the six metals supports our hypothesis. Significant increases in Ca concentrations (4 to 42 times) upon acidification resulted in little trace metal concentration increase, which suggests that most of the metals were not associated with calcium carbonate in the boiler ash (Table 5-1), and were perhaps readily available to complex with humic substances.

For the 1800 Mg ha^{-1} treatment after 7d of reaction and acidification to pH = 6, leachate Cd concentrations increased significantly ($p < 0.05$; Fig. 5-1) in the aged ash-soil profile, whereas there was no significant difference in the fresh ash-soil profile (Figs. 5-1 and 5-2). Cadmium can be adsorbed strongly onto the calcite surface, with possible formation of $CdCO_3$ (Davis et al., 1987). Thus, significant increases in Cd concentrations upon acidification in the aged ash-soil profile could have resulted from Cd release from calcite and dissolution of $CdCO_3$ formed during the weathering process. Cadmium was not mobilized in the fresh ash columns because the fresh ash was not exposed long enough to the soil and atmosphere and Cd concentrations associated with carbonate were significantly lower. Cadmium adsorption has also been shown to decrease threefold for each unit rise in pH between 4 and 7.7 depending on the concentration of other divalent

metal ions (Ca, Co, Cu, Ni and Pb, Christensen, 1984). This is why the pH in this study was not reduced below 6.

Metal concentrations in the second leachates after 35 d of reaction from the same ash-soil columns were lower than those from the first leaching after 7 d of reaction (Figs. 5-3 and 5-4), indicating most soluble metals had been leached out from the ash-soil columns during the first leaching event.

Conclusions

The results from this column study strongly suggest that acidification of wood ash following application to soil is not desirable because of increased metal (Cd, Ni, Se and As) leachability. This was probably a result of calcite dissolution and subsequent release of adsorbed metals like Cd. On the other hand, our results suggest that acidification of ash before application to the field greatly reduces metal solubility and leachability with the exception of Cd. Reduced metal mobility was mainly achieved through reduced organic acid solubilization upon acidification. This is of practical significance because the producers of wood ash have the option of acidifying their ashes before or during land application of the ash to minimize metal leaching in soils. Land application must however be done with caution (low rates recommended) as the environmental consequences due to metal loading to soils may be even worse than those of direct leaching to groundwater.

CHAPTER 6
EFFECTS OF HUMIC AND FULVIC ACID ON TRACE METAL LEACHABILITY IN AN ASH-AMENDED SOIL (I) CU AND NI

Introduction

The mobility of heavy metals in soils has been investigated extensively using soil columns under both saturated and unsaturated conditions (Camobreco et al., 1996; Madrid and Diaz-Barrientos 1998). However, these studies have mainly focused on natural soils with low volumes of amendments or pure metal salts applied to non-polluted soils. Very little research has been done on the release of heavy metals from wood ash amended soils and their potential to pollute groundwater supplies.

Factors that affect the dissolution and / or release of metals from ash and metal availability for plant uptake include soil pH, cation exchange capacity (CEC), and the amounts of organic matter and hydrous Fe, Al and Mn oxides found in the amended soil (Oden et al., 1993).

Soil organic matter plays an important role in the retention and transport of heavy metals in soils due to the tendency of transition metal cations to form stable complexes mostly organic ligands and due to the significant impact of organic matter on the CEC of the soil (McLaren and Crawford, 1973; Stevenson, 1994). The role of organic matter and colloidal complexation of metals as well as the transport and dispersal of these complexes

in the subsurface has been demonstrated by many authors (McCarthy and Zachara, 1989; Puls and Powell, 1992; Sheppard et al., 1980). In contrast to a simple exchange phenomenon where retention is determined by valence and ionic radius, the selectivity by organic matter depends on the specific electrochemical and structural properties of the ligand and metal ion. Stevenson (1994) suggested that at least four mechanisms were involved in humic substance adsorption and these include (1) physical adsorption, (2) electrostatic attraction, (3) hydrogen bonding, and (4) coordination complexes.

Copper generally reacts with organic matter by forming stable coordination complexes rather than by forming compounds via hydrogen bonding or electrostatic attraction because of its low hydration energy and low charge (Stevenson, 1994). Nickel, on the other hand, associates with organic matter to a lesser extent and complexes mostly with inorganic materials (Hickey and Kittrick, 1984). The high pH associated with the large amounts of ash applied in the current study and its potential to solubilize and mobilize organic matter make organic-matter-facilitated contaminant transport a potentially significant mechanism for the conveyance of both these metals

The chemical nature of organic matter has not been fully characterized yet, but it is generally accepted that the fulvic acid fraction of soil organic matter reacts strongly with some metals (Schnitzer, 1978). Schauberg et al. (1980) suggested that the fulvic acid fraction that reacted with metals in sewage sludge amended soils resembled that from natural soil organic matter more than that extracted from sewage sludge. Our study will establish whether this also applies to wood ash.

Insoluble organic matter effectively inhibits plant uptake of those metals (such as Cu) which bind strongly with organic matter by taking them out of soil solution thereby

preventing diffusion of these metals to plant roots. In a study of 24 British soils, McLaren and Crawford (1973) concluded that the majority of "available" Cu exists in an organically bound form. Organic matter is generally insoluble (stable) under low pH conditions. High pH conditions promote the dissolution of organic matter, thus keeping solution concentrations of DOC and metal-DOC complexes high (Sparks, 1995). The bonds that hold organic material to inorganic components are disrupted and acidic components of organic matter are converted to their soluble salt forms under alkaline conditions. Soluble organics raise the carrying capacity of soil solutions for Cu and other metals at certain pHs by forming soluble metal-organic matter complexes (McBride, 1995; Stevenson, 1994).With time, decomposition reduces the levels of soluble organics and total dissolved metals stabilise at lower levels and this ultimately reduces metal bioavailability.

Solution salinity affects the solution ionic strength and a plethora of other chemical reactions. The surface area blocked by a particle deposited on a spherical collector decreases as the ionic strength is increased and is generally several times smaller than the projected area of the particles. Variations in the magnitude of the excluded area may be in part responsible for the release (mobilization) of colloidal particles from stationary mineral grain surfaces commonly observed following a reduction in ionic strength. Daylin et al. (1995) suggested that ionic strength influences the dynamics of colloidal deposition and transport (in our case, organic matter-metal complexes) in heterogeneous porous media by controlling the range and magnitude of interparticle forces. McCarthy and Zachara (1989) observed that colloidal deposition within the soil matrix is influenced by interparticle attraction-repulsion which depend on ionic strength and the prevailing process (attraction or repulsion) is determined by pH and nature of

sorbing surfaces. The high salinity of the samples in this study and the high pH they induced in our system had significant implications on this relationship.

Previous studies on the ash in this study have shown that the leachability of metals to be highly correlated with DOC leaching from the soil (Chirenje and Ma, 1999). The leachability of trace metals was lowered by acidification of the soil columns which reduced the solubilization and subsequent mobilization of organic matter from these profiles. Therefore, the objectives of this investigation were to study the role of the organic acids in Cu and Ni leaching, in particular the role of humic acid (HA) and fulvic acid (FA) in the solubilization and leaching of Cu and Ni, and to determine the effects soil from different horizons on Cu and Ni dissolution and leachability from ash.

Materials and Methods

Column Set Up

The soil used for this study was an acidic fine sand (typic quartzipsamment) as described in Chapter 3. The ash used was generated at the same plywood plant in Hawthorne, Florida, where the ash for the field monitoring and acidification studies was obtained. Two sets of column studies were conducted. For the first set, three 0.2 m long high density polyethylene (HDPE) columns with 0.015 m internal diameter were packed separately with (i) 5.3g ash (ash only), (ii) 5.3g ash mixed with 14g of soil from the A horizon (ash + A), and (iii) 5.3g ash mixed with 14g A horizon overlying 5.2g of soil from the spodic horizon (ash + A + Bh). This corresponded to an ash application rate equivalent to 900Mg ha^{-1} (packed to field bulk density). For the second set, the same size

columns were uniformly packed with 5.3 g of ash. The columns were set up as described by Nielson and Biggar (1961). Marriot beakers, set to maintain a constant head of leaching solution under a constant suction, were used to maintain a suction of about 0.10 m to control the flow of the leaching solution throughout the study (Fig. 6-1). The leaching solution inlet was made from a porous glass frit with a very high air entry value and pore size of 10 to 15μm (Aldrich, Inc., Milwaukee, WI). Another glass frit was used at the bottom of the column giving an effective pore size of 0.2 μm for the filtrate. The soil or ash in the column was packed carefully to ascertain that there was good contact between the material and the fritted glass membrane. The leaching solution in the first set of columns

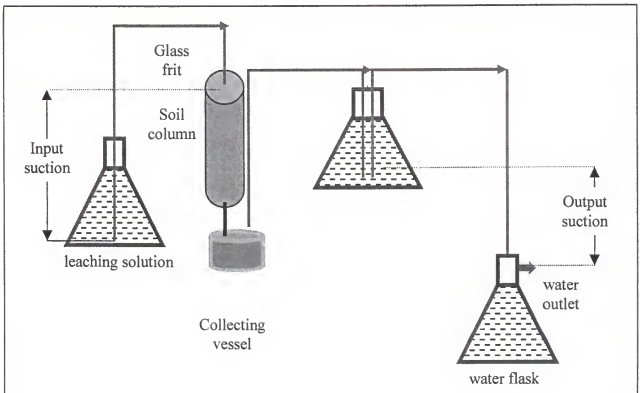


Figure 6-1. The set up of the leaching experiment (under unsaturated conditions).

was deionized water applied at a rate of one pore volume in three days (to compare the effects of soils from different horizons on the leachability of heavy metals). Although efforts were made to ensure smooth and constant flow, flow rate in these columns also depends on outside barometric pressure and temperature.

The second set of columns used three different leaching solutions, HA, FA and a combination of the two acids (HAFA) adjusted to pH 5.6 to leach the ash in columns. The pH of the acids were adjusted to the pH of the soil which was also very close to the pH of the deionized water used in the first set of columns. Fulvic acid, HA and HAFA extracted from the top soil (A horizon) of our field application site were used to leach the ash columns to distinguish the effects of these individual acids on the ash. This eliminates other factors that may have been introduced by the presence of soil. The use of organic acids from our site in place of commercial reagents allows us to get results that are specific to the conditions at our system. The comparison of results from these two experiments sheds some light on the effect of different organic acid fractions on different metals.

The concentrations of Cu and Ni that were retained by the soil was determined by digesting 0.5 g of soil in 10 mL HNO_3 acid in a microwave using EPA method SW 846-3051. The resulting solution was filtered and made up to 100 mL and analyzed the same way the leachates were analyzed.

Sorption and desorption curves for the soil were also determined. For sorption, 1g of air dry surface soil was weighed into a nalgene bottle and concentrations of Cu and Ni double the range of equivalent amounts added by the ash per gram of soil in a field profile were added as nitrate salts. The solutions were shaken for a period of 16 hours, filtered

and analyzed for Cu and Ni. Curves were then developed for the amounts in solution for each concentration. For desorption, 1 and 2g ash samples were added to containers and 20mL of deionized water was added. These solutions were then shaken and a series of samples were taken after 0, 0.02, 0.2, 0.5, 1, 2, 6, 12, 24 and 48 hours. Curves depicting desorption with time were then developed.

Chemical Extraction and Analyses

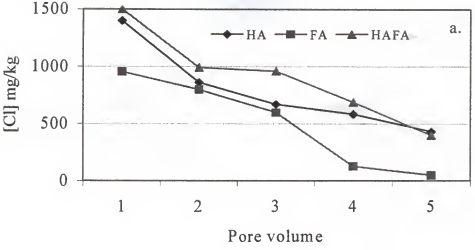
The organic matter fractions used in this study were extracted using the method described by Schnitzer (1969). One gram of soil was shaken in 0.1N NaOH, filtered and acidified of the extract to a pH < 2 using 2N HCl. The soluble material (FA) was separated from the coagulate (HA) by centrifugation. Humic acid was brought into solution and both solutions were adjusted to a pH of 5.6. The third extract was a mixture of both fractions (HAFA) and was extracted by 0.1N NaOH and adjusted to pH 5.6 using 2N HCl.

Concentrations of total Cu and Ni in the leachates were determined directly using a Perkin Elmer SIMAA 6000 graphite furnace atomic absorption spectrophotometer. Other elements were determined using a Thermo-Jarrell-Ash 61E Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES). The pH and electrical conductivity were determined using the Accumet Model 20 pH / conductivity meter (Fisher Scientific). Total carbon and DOC were determined on a Shimadzu TOC 5050 carbon analyser.

Results and Discussion

Chloride (Cl^-), which was present in large concentrations in our ash, was used as a tracer in our columns (Fig. 6-2). Over 99% of the chloride had leached out after the third pore volume in the water leached columns. The retardation in Cl^- leaching was probably due to the low solution to solid ratio and the lack of complete contact between all surfaces with flowing water in this unsaturated set-up. The increased delay in the columns incorporating the Bh horizon (87% Cl^- leached out by the third volume) was possibly due to coprecipitation in the organic layer. There was a significant reduction in hydraulic conductivity in these columns due to the clogging of pores in the spodic horizon and this may have reduced Cl leaching. In the organic acid leached columns, an average of 90% Cl^- had leached out by the end of the fourth pore volume. This may be explained by the considerable precipitation that took place in these columns. Chloride may have co-precipitated with DOC.

The soil used in this experiment did not adsorb significant amounts of Cu as shown by the sorption curves (Fig. 6-3). Significant amounts of Ni (up to 25%) were sorbed mainly because the relative Ni concentrations available in the ash were lower than those of Cu, therefore any applied Ni that went towards satisfying the mineralogical demand of the soil matrix had a noticeable effect on the different Ni fractions (Fig. 6-3). Batch studies also showed that 95% of the water soluble Cu and Ni in this batch study were desorbed from ash into solution within 12 hours. Continuous shaking over a period of 48 hours did not lead to increased desorption (data not shown). The relative amounts of water-soluble Cu and Ni in the batch experiment were much higher ($p < 0.05$) than the amounts leached in the column



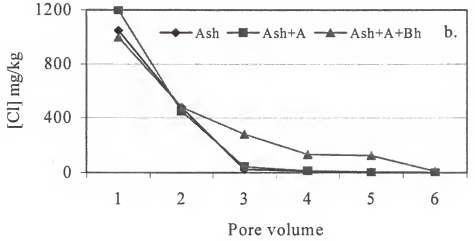


Figure 6-2. Variation of Cl concentrations in the first few pore volumes of the different columns used in the study. The legend in 6-2a represents the leaching solution where boiler ash is the column material while that in 6-2b represents the column material, deionized water being the leaching material.

study. This was probably due to the perturbation due to shaking, higher solution to solid ratio, and longer exposure duration of solution to the solid matrix allowing more metals to dissolve. Dynamic equilibrium may have been reached after relatively lower metal

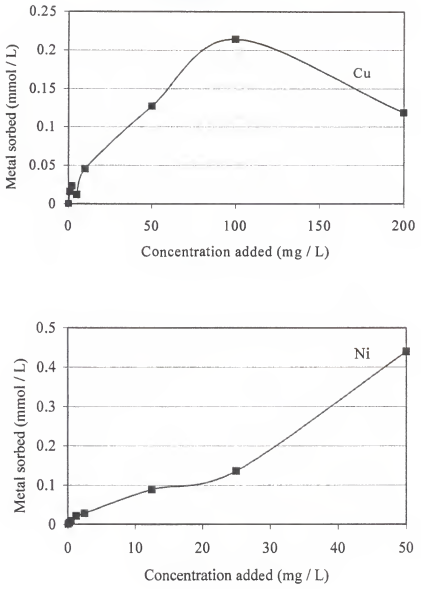


Figure 6-3. Sorption curves for Cu and Ni developed for Hawthorne soil.

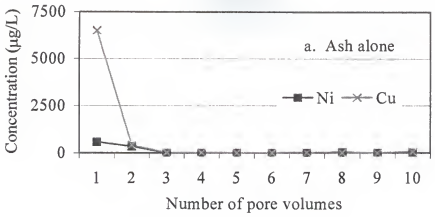
dissolution in the columns in the present study due to lower solid to solution ratio hence preventing more dissolution.

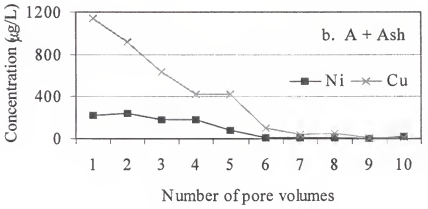
Approximately 80% of the total (water) leachable Cu and Ni was leached out by the fourth pore volume (Fig. 6-4). This represents an equivalent of two years of rainfall at

the site where this ash was applied. The average water leached Cu in the ash treatment was higher ($p < 0.05$) than that in the HA, FA, or HAFA leachates (715 μg /L compared to less than 120 μg /L in the acid leachates; Table 6-1) in the first ten pore volumes. In the water leached columns, Cu was directly dissolved from the ash matrix into solution where it may possibly have been hydrolyzed to $Cu_2(OH)_2^{2+}$ and $Cu(OH)^+$ (Baes and Mesner, 1976) which both complex with chloride to form stable but readily leachable compounds.

Less than 0.2% of the total Cu from the ash was water soluble. Of this amount, between 31 and 66 % was leached in the columns leached with water (the lower value was from the columns with a spodic horizon). The lower concentrations in the columns where the Bh was included may be due to the higher retention in the Bh layer due to the smaller particle sizes in this horizon. Fulvic acid leached columns only released less than 2%, and HA and HAFA released 10 and 12% of water soluble Cu respectively. The generally low fraction of water-soluble elements that leached may have resulted from the less intimate contact between the leaching solution and the ash/soil matrix due to the unsaturated conditions used in the experiment.

Although many researchers have reported most of the Cu in soils to be bound to organic matter (McBride, 1981), more than 80% of Cu can be complexed with chloride when chloride concentrations are sufficiently high (Doner et al., 1982). Doner (1978) showed that Cu (II) can complex with chloride to the same extent as organic matter and that the stability of the complexes depends on chloride concentration. Copper may also have been leached out as $Cu(CO_3)_2^{2-}$ and $Cu(OH)_4^{2-}$ under the alkaline conditions (McBride, 1981) of our study. However, the Cl^- complexes were more important in our study due the to presence of high concentrations of this ion (~1000 mg/L in first pore volume, Fig. 6-2).





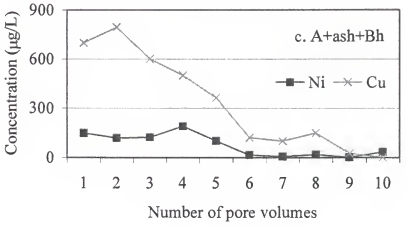


Figure 6-4. Changes in concentrations of Cu and Ni with pore volume in leachates from different horizons. Deionized water was the leaching solution in all three treatments in this set up.

The high initial concentrations of Cu in the leachates from the soil + ash columns (Fig. 6-4a) may be explained by the high initial leaching of DOC. The average DOC in first two pore volumes were 840 and 1450 mg/L for the ash + A and ash + A + Bh respectively compared to 480 in the ash only columns (data not shown). Baham and Sposito, (1986) observed an increase in the solubility of Cu in the presence of excess metal complexing ligands and postulated that this was due to the increase in stability of the metal-ligand complexes. High pH has been shown to increase the stability of these complexes due to the decrease in proton competition (Innskeep and Baham, 1983; Elliot and Huang, 1979, Davis, 1984). Organic matter solubility is also increased at high pH due to disruption of organic matter–soil inorganic phase bonds (McBride and Blasiak, 1979). Stevenson and Fitch (1981) demonstrated the complexation of Cu by humic and fulvic acids using both direct and indirect methods.

Table 6-1. Average concentrations of Cu and Ni leached in 10 pore volumes

Leaching solution	Column material	Leachate concentration (μg / L)	
		Copper	Nickel
Deionized water	Ash only	715^{a}	99.8^{a}
Deionized water	Ash + A	376^{b}	94.0^{a}
Deionized water	Ash + A + Bh	336^{b}	76.9^{b}
HA	Ash only	103^{c}	71.7^{b}
FA	Ash only	21.0^{d}	15.7^{c}
HAFA	Ash only	123^{c}	88.1^{a}

The average Cu concentrations in the first 10 pore volumes leached from the soil + ash columns were lower ($p < 0.05$) than the ash alone (715 μg / L in ash only columns compared to 376 and 336 μg / L in ash + A and ash + A + Bh columns respectively; Table

6-1). This was possibly due to the retention of some Cu in the soil matrix by some of the retained (precipitated) organic matter. Organic matter has been shown to coat the surfaces of materials it encounters in natural systems, and when the ionic strength and Fe and Al concentrations are high, adsorption is strongly favoured. For example, Davis (1982) and Tipping (1981) reported that virtually all suspended solid surfaces in water were coated by adsorbed organic matter. Although the organic matter content of our soil was very low (<1%), several researchers have shown that this has a capacity to contribute significant amounts of surface area. Peret et al. (1994) showed that 40 to 70% of the total surface area in a Rhine River sample was due to colloids < 200 nm despite the fact that this fraction accounted for only 1.5 % of the total mass.

These observations are different from the results from Chapter 5, possibly because we used a very low solution to solid ratio in the current study compared to the leaching of up to 8 pore volumes at a time under saturated conditions in the study in Chapter 5. The increased ionic strength in the current study hence favoured precipitation of DOC and reduced Cu leaching (Appendix).

Copper mobility from organic acid leached ash-columns was much lower than that in water leached ash-columns (average concentrations of Cu leached in ten pore volumes were 103, 21 and 123 for HA, FA and HAFA, respectively, compared to 715 for water; Table 6-1). This can be explained by the flocculation of Cu-organic matter complexes due to the very high ion activity in the organic acid leached columns. The average DOC in the organic acid fractions was 12.7 mg/L compared to 96 mg/L in the water leached columns. The presence of large quantities of Ca and Mg in our columns possibly increased the formation of ternary complexes and / or acted as cationic bridges between OM and soil

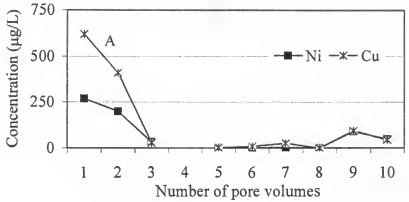
surfaces (Greenland, 1970). The reduction in Cu concentration was highest in the FA columns possibly due to the higher reactivity of these acids and hence their high tendency to flocculate faster under conditions of high ionic strength. The amount of Cu leached from the HAFA columns was approximately equal to the sum of the FA and HA suggesting that their effect may be additive (Table 6-2).

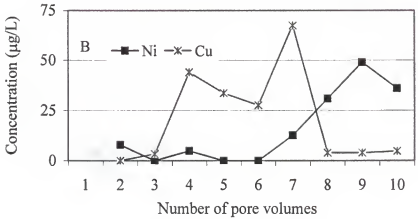
Nickel leaching in the water-leached columns was comparable to that in columns where combined fractions of HA and FA were used (99.8 μg /L compared to 88.1 μg /L; Figs. 6-4 and 6-5) possibly because the extent of Ni-DOC complexation was just as effective as the association of Ni with inorganic carbon (Table 6-2). About 9% of the total Ni in the ash was leached in the water-leached columns compared to just above 8% in the HAFA leached columns.

Table 6-2. Average concentrations of carbon fractions leached in 10 pore volumes

Leaching solution	Column material	Inorganic C	Dissolved Organic C	Total C
		---------- mg / L ----------		
Deionized water	Ash only	1160	96.0	1260
Deionized water	Ash + A	810	242	1050
Deionized water	Ash + A + Bh	1280	373	1650
HA	Ash only	907	8.00	914
FA	Ash only	985	2.60	990
HAFA	Ash only	1700	27.0	1720

The soil chemistry of Ni is relatively simple and is based on the divalent metal ion Ni^{2+}. The $Ni_4(OH)_4^{4+}$ ion has been shown to be the predominant polymer in Ni (II) solutions and salt solutions (Christensen et al., 1996). At high pH, Ni precipitates as $Ni(OH)_2$





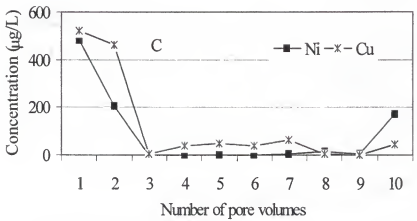


Figure 6-5. Changes in [Cu] and [Ni] with pore volume in (a) HA, (b) FA, and (c) HAFA leached columns

hence this was probably not the species responsible for Ni loss in our columns. Christensen et al. (1996) observed that at these high pHs, chloro-complexes were negligible but carbonate complexes accounted for > 90% of dissolved Ni up to concentrations of 9%. Sposito and Page (1984) made similar observations, noting that the dominant species were $NiCO^0_3$ and $NiHCO_3^+$. These species may have contributed to the high initial leaching of Ni in our columns because of the high concentrations of carbonates and inorganic carbon in our ash (Table 6-2). Wang et al. (1997) showed that Ca competes for adsorption sites with Ni, hence the presence of high concentrations of Ca and CO_3^{2-} may have led to the high Ni leachability (initial concentration in ash only 10 mg /L) in this study. Bowman et al. (1982) also noted the competition between Ca and Ni for adsorption sites.

Mixing ash with the surface soil did not increase Ni leaching although the DOC increased from <100 mg/L to 242 mg/L (Table 6-2). When the Bh horizon was included, almost 75 % as much Ni was leached. This may be due to increased adsorption due to the finer particles present in the Bh horizon or the increased leaching solution residence time in the Bh horizon columns allowed adsorption/desorption or precipitation/dissolution processes to reach equilibrium at higher values (favouring adsorption and precipitation). The amount of Ni in the HA leachate was 72 % that in the water leachate (Table 6-1). Similar to Cu, Ni concentration was much lower in the FA leachate and the amount leached by HA and FA was additive (Figs. 6-4 and 6-5).

Similar to Cu, these observations are different from the results from Chapter 5. However, since Ni does not complex with DOC to the same extent as Cu, the reduction in Ni leaching was much less than that of Cu in the organic acid leached ash columns. The reduction in Ni leaching in the acidified columns in Chapter 5 may therefore be due to other

factors that changed with the change in pH rather than the change in DOC leaching that resulted from changing the pH.

Conclusions

This study has shown that the extent of organic matter facilitated metal transport in columns depends on the mobility of the organic matter-metal complexes within the system and this mobility is in itself a dynamic process governed by variable kinetics. While the soil used in this study was sandy, the addition of ash increased soil pH creating conditions favorable to organic matter dissolution but the high ionic strength resulting from the salts in the ash also created conditions favorable for flocculation of charged particles.

Although the organic matter fractions used in this study were extracted using dilute alkali, separated into the humic and fulvic acid fractions by acidification, the extracted fractions may not have the same structural arrangement or proportions to those from other sites. The high pH that resulted from mixing ash with organic acids also has the effect of oxidising some components of the organic acids, possibly altering their reaction patterns. The heterogeneous complexing nature of the organic ligands (where opposing processes occur simultaneously in the system) may have also confounded our results. Nonetheless, we agree with Tyler and McBride (1981) who showed that in general, the prevailing soil chemical properties are more important in determining the movement of metals through soil columns than the properties of the metals themselves.

CHAPTER 7
EFFECTS OF HUMIC AND FULVIC ACID ON TRACE ELEMENT LEACHABILITY IN A WOOD ASH-AMENDED SOIL (II) AS AND CR

Introduction

Relatively few studies have investigated the leachability of oxyanions under conditions of high pH and salinity. This study examines the effect of application of high volumes of wood ash on the mobility of As and Cr. Chromium is studied here as an oxyanion because its only common stable cationic form, Cr (III), is not very mobile under normal conditions (Shupak, 1991). The more mobile and toxic Cr (VI) does not exist as a free ion but as chromate (CrO_4^{2-}), dichromate ($Cr_2O_7^{2-}$), or chromium trioxide (CrO_3^{2-}) which all behave as divalent anions rather than hexavalent cations (Kimbrough et al., 1999). This investigation is a compliment of the study in Chapter 6 where the leachability of the cationic metals (Cu and Ni) under the same conditions was determined.

As discussed previously, wood ash derives its salinity and alkalinity from wood bark processing methods and its chemical composition (principally salts and oxides of Ca, K, Fe, Al, Mn, Na, and Mg, and trace elements in lesser proportions, Pepin and Coleman, 1984). While most of the factors that affect the solubility and availability of metals from ash apply equally in the dissolution and leachability of oxyanions, their effects may be opposite due to the differences in charge between these species. The conditions under which these factors are most predominant also vary due to charge differences.

Understanding the processes governing the migration of oxyanions is essential for predicting the environmental impact of spreading wastes on land (Stumm and Morgan, 1981; Sposito et al., 1982a,b). For instance, large doses of Cr in human blood have been shown to cause chronic liver and kidney damage and tubular necrosis (Kurzel and Cetrulo, 1981). On the other hand, As has been shown to be both teratogenic and fetotoxic in humans (Kurzel and Cetrulo, 1981).

Earlier studies of the ash used in this study have shown that the leachability of its constituent elements was highly correlated with DOC leaching (Chirenje and Ma, 1999). It was suspected that there could be other factors that were being masked by this association because in general, oxyanions do not complex with organic acids to a great extent. Although organic matter in non-acid soils is much more capable of complexing with trace metals (unlike naturally acidic soil where OM is generally tied up by Al, Tyler and McBride, 1982) there may have been other factors in this experiment that affected mobility and association of this "free" OM with oxyanions.

There is very little evidence in the literature on the adsorption of Cr by organic matter. Eary and Rai (1991) showed that Cr (III) and $Cr(OH)^{2+}$ can bind to solids that have exposed negatively charged edges, e.g. surfaces of organic matter, but the pH range under which Cr (III) exists is very low and narrow. In fact, Cr (III) does not exist as a free ion above pH 3.8 and $Cr(OH)^{2+}$ does not exist in solution above pH 6.3. Since Cr (VI) commonly exists as negatively charged chromate ions, these species do not have strong affinities for any DOC, unless they are bonded through Fe or other metals like Al.

Arsenic association with organic matter has been well documented in the literature (Cullen and Reimer 1989; Xu et al, 1991). Arsenic is converted to volatile

organics through biomethylation by microbes over a wide range of pH. Takamatsu et al. (1982) reported high levels of As (III) and dimethylarsinate ($(CH_3)_2AsO(OH)$) under high pH conditions and high levels of arsenate and monomethylarsonate ($(CH_3)AsO(OH)_2$ pKa of 4.19 and 8.77) under low pH upland conditions. However, As leaching from soils is generally limited by adsorption on Fe and Al oxides and clay surfaces. The behavior of As (V) has in fact been shown to be similar to that of P due to the near similarities of the pKas of their respective acids. The successive pKas for H_3AsO_4 at 25^0C are 2.2, 6.9 and 11.5, and the corresponding values for H_3PO_4 are 2.2, 7.2 and 12.4 (Cullen and Reimer, 1989). In a study of sediments along the Xiangjiang River in China, Chunguo and Zihui (1988) showed that As was mainly bound as Al-arsenate, Fe-arsenate, Ca-arsenate, and Fe-occluded arsenate, just like P. Lesser species were soluble As^{3+}, soluble and insoluble organic As.

Similar to our first study (Chapter 6), the specific objectives of this study were to study the role of organic acids (humic and fulvic acids) in the leaching of As and Cr and to determine the effects of soil from different horizons on As and Cr dissolution and leachability from ash.

Materials and Methods

The total concentration of As and Cr in the ash was 2 and 12.5 mg kg^{-1} and this was 3 and 5 times the concentrations in the soil, respectively. The leaching characteristics of these two elements were studied because of the large amounts of ash applied in the field warranted concern about their possible toxicity.

The materials and methods were identical for those used in the Cu/Ni study (Chapter 6). It is worthwhile noting that the concentration of Cr in the sample used in the leaching study was six times the concentration determined in the main sample used in the field. Such heterogeneity is not unusual for samples that are produced in such large quantities and accumulated over a period of 2-3years. Although all precautions were taken in ensuring that the sample brought into the laboratory was thoroughly mixed and from one batch, there might have been pockets of heterogeneity within the sample. However, this heterogeneity was not observed in the other elements. As with Cu and Ni, concentrations of total Cr and arsenic in the leachates were determined using a Perkin Elmer SIMAA 6000 graphite furnace atomic absorption spectrophotometer (GFAAS).

Results and Discussion

Similar to what was done in the Cu/Ni experiment, the leaching of chloride was used to show the leaching of a non-conservative element from the columns (Fig. 6-2). If there was no interaction between the soil and the two oxyanions, their leaching patterns would have been similar to that of chloride. Although only very low concentrations were added in the batch study (as arsenic trioxide), the soil used in this experiment did not adsorb significant amounts of As (Fig. 7-1a). Considerably higher amounts of Cr, added as potassium dichromate, were adsorbed by the soil. Batch studies showed that Cr desorption was very fast and nearly 25% of the total Cr in the ash was desorbed within 6 hours of shaking (Fig. 7-2b).

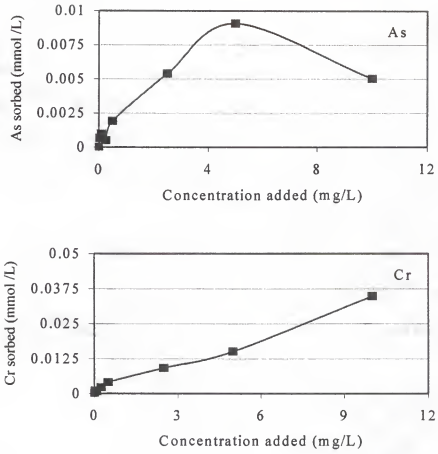


Figure 7-1. Sorption curves for As and Cr developed for Hawthorne soil.

The relative amounts of Cr and As desorbed in these batch studies was much higher than that in the column leaching experiments. Similar to the Cu/Ni study, this was possibly due to the shaking, longer contact time and exposure of more solution to ash surfaces allowing more Cr to dissolve in the batch study. Dynamic equilibrium between leaching solution and particle surfaces was possibly reached at lower absolute concentrations in the columns due to the lower liquid to solid ratios used. Up to one eighth

of the total As was also desorbed at the end of 12 hours. Continuous shaking over a period of 48 hours did not lead to any increased desorption in both elements (Fig. 7-2).

In general, the two oxyanions (Cr and As) leached faster than the cations, Cu and Ni. More than 90% of the leachable As and Cr had been leached out by the end of the third pore volume (Fig. 7-3) compared to four pore volumes in the case of Cu and Ni (Fig. 6-3). The increased concentration in the fourth pore volume leachate was due to the delay in sampling. A period of two weeks was used as the interval compared to 3 days in all the other samples and this gave As and Cr more time to dissolve.

Table 7-1. Average concentrations of [†] As and Cr leached in the first 10 pore volumes

Leaching solution	Column material	Leachate concentration (μg / L)	
		Arsenic	Chromium
Deionized water	Ash only	23.0[a]	247[b]
Deionized water	Ash + A	21.6[a]	300[c]
Deionized water	Ash + A + Bh	36.6[b]	574[e]
HA	Ash only	57.6[d]	143[a]
FA	Ash only	42.3[c]	465[d]
HAFA	Ash only	44.9[c]	487[d]

[†] More data presented in Tables A6-8 in the Appendix

The average concentration of water-leached Cr in the ash columns was lower than that leached from the ash-soil mixture in the first ten pore volumes (300 μg L^{-1} compared to 247 μg L^{-1}; Table 7-1).

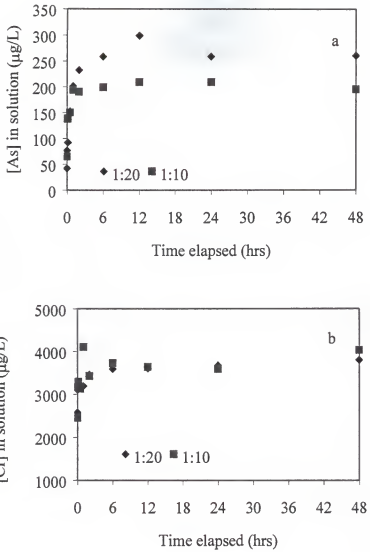


Figure 7-2. Desorption curves for the soil using two dilution ratios for As and Cr. The concentrations of As and Cr in solution represent the concentrations of the two elements that dissolved from the ash matrix.

The mixing of ash with soil possibly exposed Cr to more reaction sites on the soil surfaces hence promoting more dissolution. Almost 50% more Cr was leached from the column consisting Ash + soil + Bh horizon possibly due to the dissolution

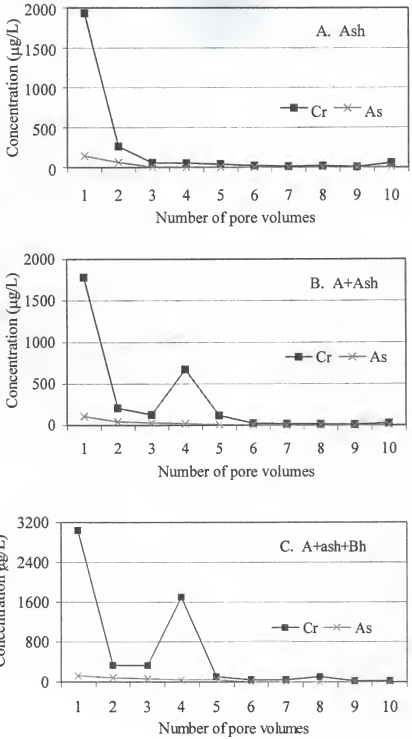


Figure 7-3. Changes in concentrations of As and Cr with pore volume in water leachates

kinetics of Cr and the change in water flow dynamics induced by the presence of the Bh horizon. Water flow in these columns was slower than that in the other columns and hence the leaching solution had more contact time with the matrix leading to equilibrium being reached at a higher solution Cr concentration than in columns where solution passed through quickly. The lower flow rate may have also made it possible for the leaching solution to reach surfaces not easily accessible to faster moving solutions. The relative fraction of water-soluble Cr leached in our columns was more than that of Cu and Ni (Chapter 6) suggesting that Cr did not react with column constituents to the same extent as Cu and Ni.

Although Cr (III) is the most stable form of Cr under acidic conditions common in most natural soils and sediments, the combustion process from which our ash was produced and the high pHs involved tend to favour the oxidation of Cr (III) to the more mobile Cr (VI). The dissolved species of Cr (VI) (hydrochromate ($HCrO_4^-$), dichromate ($Cr_2O_7^-$) and chromate (CrO_4^{2-}) are mobile in soils and their leaching can be coupled to that of any of the major cations that were present in the ash (Bartlett and James, 1979; James and Bartlett, 1983). The leached Cr in this study must therefore be due to these Cr (VI) forms.

There was less Cr leaching in the HA than the FA treated columns (143 versus 465 $\mu g\ L^{-1}$, Table 7-1). Humic acids are less reactive than the smaller sized and more surface reactive FA. Our postulation in the Cu/Ni study that the organic acids precipitated out at these high ECs applies here as well. Chromate was easily leached in the FA columns because it was not associated with any of the FA that flocculated and stayed in the soil matrix. In the HA columns, leaching was probably limited by the element's own solubility

and leaching characteristics of the column. In fact, the chromate species has been shown to react with humates, and this may explain the low leaching in HA leached columns.

Water leached columns had lower Cr concentrations than FA and HAFA leached columns (247 μg/kg compared to 465 and 487 μg/kg respectively, Table 7-1). As discussed earlier, FA-leached columns had lower Cr concentrations due to the retention of Cr with humates in the column. Mixing ash with soil only led to slight increases in Cr leached while the inclusion of the Bh horizon slowed leaching rate and increased the total amount of Cr leached. The two columns that contained soil had significantly higher DOC concentrations ($p < 0.05$). The increase in Cr leaching in these columns must have been purely coincidental because Cr leaching in the columns where DOC was retained in the matrix was not reduced. In fact it was increased in the case of FA-leached columns. The behaviour of Cr in this study was different from that in Chapter 5. Similar to the Cu/Ni study, the difference must come from the changes in solution chemistry, namely changes in flow velocity and solution to solid ratio led to increase in ionic strength which in turn induced precipitation of DOC fractions.

Table 7-2. Average concentrations of carbon fractions leached in 10 pore volumes

Leaching solution	Column material	Inorganic C	Dissolved Organic C	Total C
		---------- mg / L ----------		
Deionized water	Ash only	1160	96.0	1260
Deionized water	Ash + A	810	242	1050
Deionized water	Ash + A + Bh	1280	373	1650
HA	Ash only	907	8.00	915
FA	Ash only	985	2.60	990
HAFA	Ash only	1700	27.4	1720

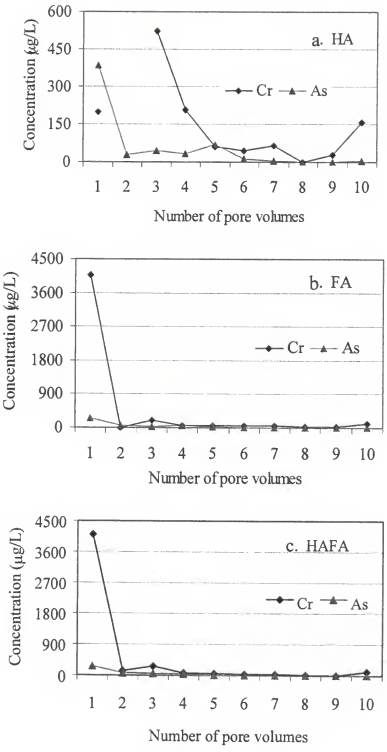


Figure 7-4. Changes in the concentrations of As and Cr with pore volume using different leaching solutions.

The average water leached As was lower than that leached by HA and FA (23 $\mu g\ L^{-1}$ compared to above 40 $\mu g\ L^{-1}$; Table 7-1; Figs. 7-3 and 7-4). The relative amount of As leached in our columns was lower than that of Cr ($p < 0.05$), suggesting that Cr was relatively more soluble from our ash. Batch studies confirmed this observation. Mixing ash with top soil did not change the amount of As leached despite the increase in the amount of DOC leached (Table 7-2). In studies conducted on two wetland sites, Kalbitz and Wennrich (1998), noted that As was only marginally mobilized by DOC because of the low pH in the soil in one site and highly mobilized in the site where the pH was slightly higher. The percentage of DOC was also much higher at the second site. The inclusion of the Bh horizon in our study led to an increase in the amount of As leached. This may be largely due to the change in water flow properties as the inclusion of the Bh horizon increased the contact time between leaching solution and matrix due to the lower pore water velocity.

The HA fraction leached more As than the FA fraction (Table 7-1), possibly due to higher association of As with FA than HA. There was negligible microbial activity in these columns because ash had a very high pH and salt content (data not shown) and therefore both As immobilization into the organic fraction or volatilization through methylation were not significant. The HAFA leached columns leached numerically lower As than the HA fraction alone but this was not statistically significant (Fig. 7-4). All acid leached columns had higher As concentrations than water leached columns, suggesting that there was minimal interaction between As and the organic acids. In fact, the preponderance of negative charge in the acid leached columns may have led to repulsion of the negatively charged As species leading to increased leaching. Breslin and Duedall (1983) found that both As (V) and As (III) leached from fly ash, but arsenate was predominant (77%). Turner

(1981) noted that As was initially leached as As (III) in his study but As (V) increased with leaching and postulated that adsorption or catalytic oxidation was responsible for this. This might be occurring in our columns due to the high levels of Mn oxides present (Table 2-1). Fulvic acid has also been shown to have a higher impact on the desorption isotherms of As(V) than As(III) (Xu et al., 1991).

Conclusions

This study showed that although both As and Cr move in the soil as oxyanions, the extent of their solubility very much depends on their individual chemical properties and how they interact with the soil matrix. Both oxyanions leached faster than the cations studied in Chapter 6 showing that they had less interaction with the solid matrix. This study had the same limitations as the Cu/Ni study. The extremely high pH of the leaching solution, coupled with the high ionic strength of the leaching solution may have masked some of the relatively simple but important reactions governing metal solubility and subsequent leaching in our columns. Therefore, it is extremely difficult to isolate the predominant mechanisms against such a background.

CHAPTER 8
GREENHOUSE STUDY OF SLASH PINE RESPONSE TO FERTILIZER IN A WOOD ASH-AMENDED SOIL

Introduction

Burning wood trimmings, chips and tree bark to provide energy generates large quantities of ash at papermill, plywood and some power generating plants (Huang et al., 1992). Wood ash generally consists of salts, oxides and hydroxides of Ca, Mg, and K, plus low quantities of micronutrients and trace metals which are extracted from the soil during tree growth (Hakkila and Kalaja, 1983; Naylor and Schmidt, 1986). These elements become more concentrated in the ash due to loss of tree bark biomass during combustion. Some wood ashes also contain large quantities of Na, from sodium hydroxide used in the processing of tree bark, making these ashes highly saline as well.

The use of ash for agronomic purposes (both as a liming and fertilizer material) is rapidly gaining popularity. Many studies have shown that wood ash can be beneficially applied to forest soils both as a liming agent (Lerner and Utzinger, 1986; Naylor and Schmidt, 1986; Muse and Mitchell, 1995) and as a source of nutrients (Campbell, 1990; Naylor and Schmidt, 1989; Ohno and Erich, 1990). Pohjonen (1981) reported considerable positive effects of wood ash on fast-growing forest trees, *Salix spp*, in Finland. Unger and Fernandez (1990) reported significant increases in concentrations of

exchangeable bases (Ca, K, Mg and Na) in ash amended soils. Ohno and Erich (1990) noted that the average nutrient release from Maine and New Hampshire wood ashes was 5.7% for P, 40% for K, 48% for Mg, 74% for Ca, and 16% for Na after mixing and incubating the ash with sandy loam soils.

Ash can also have an impact on soil physical properties, because it is comprised primarily of silt and clay-sized particles. Ghodrati et al. (1995) reported an increase in soil water-holding capacity from 12 to 25% after addition of 30% fly ash. However, wood and fly ashes from different facilities vary widely in physical and chemical properties due to differences in furnace temperature, duration of combustion period, priming method, and nature of the tree bark (Campbell, 1990; Erich, 1991). This makes it difficult to draw conclusions solely from other research.

New and published research has only dealt with low application rates of wood ash. As a result, trace metal toxicity to plants and the dangers posed to nutrient availability (especially that of P, N and Mn) and assimilation by the high pH and salinity induced by wood ash have not been of major concern.

The pressing need to increase the efficiency of land application, save costs, and maximize the efficiency of resource utilization has led some companies to investigate the impact of these high rates. Hence the concerns associated with land application have shifted from those of merely meeting nutrient and liming rates to making sure that land application is sustainable and not harmful to crops and plants which are meant to benefit from it.

The objectives of this study were to determine the effects of fertilizer application on slash pine nutrient uptake and slash pine biomass accumulation in a pot study of soil

amended with two high rates of wood ash. The effects of ash on slash pine growth, soil chemical properties and soil moisture retention were also evaluated.

Materials and Methods

Wood Ash and Soil Sampling

The ash used in this study was the same ash used in the field study and it was generated from the same plywood plant in Hawthorne, Florida. The fresh ash produced from the plant was hauled to a nearby site, compacted and stored in piles approximately 8m high and 40m in diameter without cover protection (i.e. the ash was subject to natural leaching and weathering) for a period of two years (from 1993 to 1995). The ash was applied to an acidic fine sand (Typic Quartzipsamment) with a spodic horizon below 2 m, in December of 1995 at rates of 0, 900 and 1800 Mg ha^{-1} as described in Chapter 3. A completely randomized design was used for the three field treatments (0, 900 and 1800 Mg ha^{-1} ash application), with three replicates. It must be noted that these application rates (8-15 cm layers) far exceed normal land application rates. As described earlier, the primary consideration in applying these large amounts was to improve soil moisture retention with little attention being paid to chemical properties. The ash was incorporated and mixed with the surface soil by disk plowing to a depth of 47 cm and the ash-soil treatments underwent natural leaching for about 1½ years before slash pine seedlings were planted.

In August of 1997, soil samples were collected to a depth of 40 cm from each of the three replicate treatment sites and mixed to obtain a composite sample for this study.

The chemical composition of the ash-amended soil and the control, after 1½ years of natural leaching in the field, are shown in Table 8-1.

Table 8-1. Total elemental concentrations of the control soil and ash-amended soils after 1½ years of leaching

Element	0 Mg ha^{-1}	900 Mg ha^{-1}	1800 Mg ha^{-1}
	---------- g kg^{-1} ----------		
Ca	0.10	3.16	7.24
Na	0.04	0.55	0.86
Mg	0.03	0.35	0.74
K	0.03	0.13	0.25
Al	2.00	2.46	2.48
Fe	0.80	1.27	1.47
P	0.10	0.17	0.28
	---------- mg kg^{-1} ----------		
Mn	14.0	32.7	65.3
Zn	0.01	0.02	0.05
Pb	1.30	1.29	2.62
Cu	1.00	2.34	5.71
Se	0.70	0.03	0.11
Ni	5.00	1.24	1.85
Cr	4.00	3.97	4.65
pH	5.60	8.60	8.80
EC (dS m^{-1})	2.00	12.0	13.0

Greenhouse Setup

Two kilograms of soil from each treatment (0, 900 and 1800 Mg ha^{-1}) were placed into 0.16 m diameter pots, giving an approximate bulk density of 1400 kg m^{-3}. To determine the impact of fertilizers on tree growth, a control and two fertilizer regimes (NPK, and NPK + Fe/Mn/Cu) were applied to each treatment. The soil and fertilizer were thoroughly mixed in pots, resulting in a total of nine treatments with each treatment

having four replicates for a total of 36 pots (3 ash application rates x 3 fertilizer treatments x 4 replications). Two 9-month old slash pine seedlings of known height were planted in each pot for a total of 72 trees in the experiment. Fertilizer rates equivalent to the commonly used 80, 90, and 80kg ha^{-1} (w/w) of N, P and K respectively and 10 kg ha^{-1} (w/w) Fe, Mn and Cu were applied to the pots. Fertilizer sources were $(NH_4)_2HPO_4$, (1:1:0) and K_2HPO_4 (0:1:2) and sulfates for the micronutrients. The trees were watered and weeded as needed for 10 months. At the end of the 10-month growth period, tree heights were measured and the trees were harvested and separated into three portions: roots, stems and needles. The fresh and oven-dry weights of each portion were determined, and each portion was then ground and analyzed for N, P, K, Ca, Na, Mg, and micronutrients.

Chemical Analyses

The calcium carbonate equivalent (CCE) of the ash was determined according to the method by Erich and Ohno (1992a). The only modification to this method was that the samples were not heated because preliminary studies showed that heating did not make any difference in our samples. The pH of the soil and wood ash was determined using a 1:2.5 solid to water ratio. Concentrations of N, P, K, Ca, Mg, Na, Cu, Fe, Mn, and Zn in plant tissues were determined by the wet digestion method using H_2SO_4 with Se as a catalyst. Plant tissue (0.2 g) was weighed into a 50 mL digestion tube. Approximately 2 mL of concentrated H_2SO_4/Se (made by dissolving 5g Se powder in 1 L of concentrated H_2SO_4 on a hotplate) were added and the paste was digested in a block at 340°C until the solution was clear (3 hours). The solution was brought to volume using

deionized water and the supernatant was analyzed for metals using a Thermo-Jarrell-Ash 61E inductively coupled plasma atomic emission spectrophotometer (ICP-AES). Phosphorus concentration was determined using the molybdenum blue method (Watanabe and Olsen, 1965) and N concentration was determined using a modified Kjeldahl method (Bremner and Shaw, 1955) on an autoanalyzer. Extractable soil Ca, Mg, K, and P were estimated by extracting the soil with 1M NH_4OAc (Schollenberger and Simon, 1945) and extractable soil micronutrients (Cu, Fe, Mn and Zn) were extracted with a DTPA solution (Haq and Miller, 1972). Elemental concentrations were determined by ICP-AES.

Results and Discussion

Changes in Soil Chemical Properties

A detailed discussion of the changes in soil chemical properties is given in Chapters 3 and 4. Although the CCE of the ash was determined to be 20%, the high alkalinity of the ash (pH = 11.6) and extremely high application rates (900 and 1800 Mg ha^{-1}) used in this study resulted in significant elevation of soil pH. The soil pH in the field increased from 5.6 in the control plots to above 9.4 ($p < 0.05$) in the ash amended plots after about six weeks, but this had decreased to $\approx$ 8.6 after eight months (Chirenje and Ma, in press). The pH did not go below 8.6 even after 20 months of natural leaching in the field, primarily due to the presence of calcite in the soil. Other researchers have also observed pH increases in ash-amended soils (Clarholm, 1994). However, these increases were generally less than one pH unit (Naylor and Schmidt, 1989; Unger and Fernandez,

1990). This variation is due mainly to the differences in ash application rates, with pH increases of three units not uncommon for natural systems where severe burning has been shown to increase the pH of surface soil by up to three units (Ulery et al., 1993).

Significant increases in concentrations of nutrients and trace metals were observed immediately after ash application ($p < 0.05$). However, considerable amounts of nutrients and trace metals were leached by the ≈ 2500 mm of rainfall between ash application and sampling time. For example, Ca concentrations initially increased to 8.5 and 15 g kg^{-1} but subsequently decreased to 3.2 and 7.2 g kg^{-1} for the 900 and 1800 Mg ha^{-1} application rates respectively (Table 8-1). Concentration decreases for the more soluble salts, e.g. Na, were even more pronounced. Sodium concentrations fell from an initial value of 1.6 g kg^{-1} after application to ≈ 0.5 g kg^{-1} after 20 months (Table 8-1). There was still considerable elemental elevation in the soils, especially in the 1800 Mg ha^{-1} treatments, where Ca, Na, and Mn concentrations were approximately 80, 20 and 7 times their concentrations in the control soil. The electrical conductivities of these treatments were also six times higher than for the control soil.

Tree Growth

The impact of different fertilizer treatments on slash pine after 10 months of growth in an ash-amended soil was also determined. Tree height responded positively to additions of NPK and NPK+Mn/Fe/Cu in all pots, with the control soil having the greatest response ($p < 0.05$, Fig. 8-1a). This is in agreement with results from Unger and Fernandez (1990) who reported that red maple (*Acer rubrum, L*) seedlings receiving N

and K had numerically higher average stem height than the controls. Ash application reduced tree height by 36% without fertilizer addition ($p < 0.05$). Other researchers have observed the opposite effect using lower ash application rates. For example, Ferm et al. (1992) reported significant increases in tree growth for Scots pine (*Pinus sylvestris*) during periods of up to 13 years after ash application at 20 Mg ha^{-1}. Addition of NPK+Mn/Fe/Cu to the ash-amended soils lessened the reduction in tree height to only 15% in this study ($p > 0.05$, Fig. 8-1a).

Reduction in tree height may have been due to the extremely high salt content of the ash-amended soil. For example, Na concentrations in the ash-amended soils were 0.55-0.86 g kg^{-1}, which were many orders of magnitude greater than the value for the control soil of 0.04 g kg^{-1} (Table 8-1). This may have negatively impacted growth factors such as nutrient uptake and assimilation (Sparks, 1995; Huang et al., 1992). The 1800 Mg ha^{-1} treatment responded to the NPK treatment more than the 900 Mg ha^{-1} ($p < 0.05$), further demonstrating the salt effect. The 900 Mg ha^{-1} treatment and control both responded to the addition of Mn/Fe/Cu, while the 1800 Mg ha^{-1} did not.

The 900 Mg ha^{-1} treatment apparently did not provide enough nutrients (P and K) for tree growth under the conditions of this study. There were P and K deficiency symptoms for the 900 Mg ha^{-1} treatment and the unfertilized controls which disappeared upon NPK fertilization. The response of total plant biomass to the treatments was similar to the tree height response (Fig. 8-1b); i.e. addition of ash reduced plant biomass, but addition of fertilizer increased plant biomass with ash-amended soil having the greater response. Unlike tree height and plant biomass, fertilizer addition significantly decreased root weight ($p < 0.05$, Fig. 8-1c) and hence reduced net gain in plant weight for the

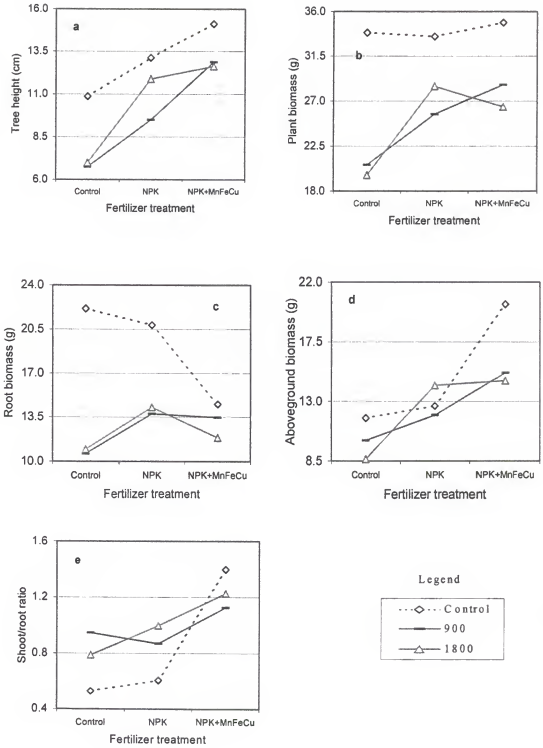


Figure 8-1. Pine tree growth, biomass, and shoot / root ratio after 10 months

control (Fig. 8-1b). The response of aboveground plant biomass was similar to tree height response (Fig 8-1d).

The total biomass response can be misleading if the responses of shoots and roots are not separated. Berry (1985) did not observe any differences in total fresh biomass of pine seedlings amended with different types of wood ash and sludge amendments. No separation was made in that experiment, however, so it was difficult to determine what the treatment effects were. In our experiment, root biomass for the controls, where no fertilizer was added, was the greatest, decreasing with addition of NPK and decreasing further with the addition of NPK+Mn/Fe/Cu (Fig 8-1c). Trees in ash-treated pots had less root proliferation, possibly due to the supply of Ca, K, P, Fe, Mn and Cu provided by the ash. These plants did not have to spend energy and carbon in developing extensive root systems, as nutrients were abundant (Etiegni et al., 1991; Patel et al., 1993). The control plots did not have these benefits, so plants in the control pots developed extensive root systems to provide more surface area for nutrient uptake. The slight decrease in root weight for the 1800 Mg ha^{-1} pots may actually be a manifestation of negative root response to excessive micronutrient concentrations (a possible micronutrient phytotoxicity).

For the control treatments, the aboveground biomass (Fig 8-1d) increased more with fertilization than did the roots ($p < 0.05$, Fig 8-1e). This shows that the soil used in this study had inherent micronutrient deficiencies, thus making it possible for us to compare fertilizer and ash effects.

These results showed the response of slash pine under well-controlled greenhouse conditions. In a complimentary field study, Vest et al. (1999) showed that slash pine tree

mortality after one year was 39 and 78% in the surface plots, 9 and 10% for the 900 and 1800 Mg ha^{-1} subsurface plots respectively compared to 31% for the control. However, their experiment was affected by the long drought and fire outbreak in the summer of 1998 in Florida. Nonetheless, the treatments showed that the subsurface plots had lower mortality ($p < 0.05$) due to the buffer provided by the re-applied surface soil. By the time the roots reached the ash impacted soil, the plant had established its stand firmly. The high mortality in the controls was most likely due to water stress and nutrient limitations.

Macronutrient Uptake

Concentrations of Ca, Mg, K, and P in the ash-amended soil were approximately 70, 20, 8, and 22 times greater than those for the control soil (Table 8-1). Therefore, increased plant uptake of these elements was expected for the ash-amended soil. Calcium uptake generally increased with addition of NPK and NPK + Mn/Fe/Cu in the control ($p < 0.05$, Fig 8-2a). This was possibly a result of increased plant needs for cellular structural integrity as plant growth increased. Plants in the ash-amended soil had significantly higher Ca uptake due to greater Ca supply from the ash. This is in agreement with Ohno and Erich (1990), who determined that an average of 74% of applied Ca from six wood ashes was plant-available in 12 Maine soils. There was no significant difference in Ca uptake between the 900 and 1800 Mg ha^{-1} treatments ($p > 0.05$), so plant Ca requirements may already have been met by the 900 Mg ha^{-1} ash treatment. The low correlation between tissue uptake and plant-available Ca in soil was possibly due to oversupply of Ca by the ash, especially for the 1800 Mg ha^{-1} treatment.

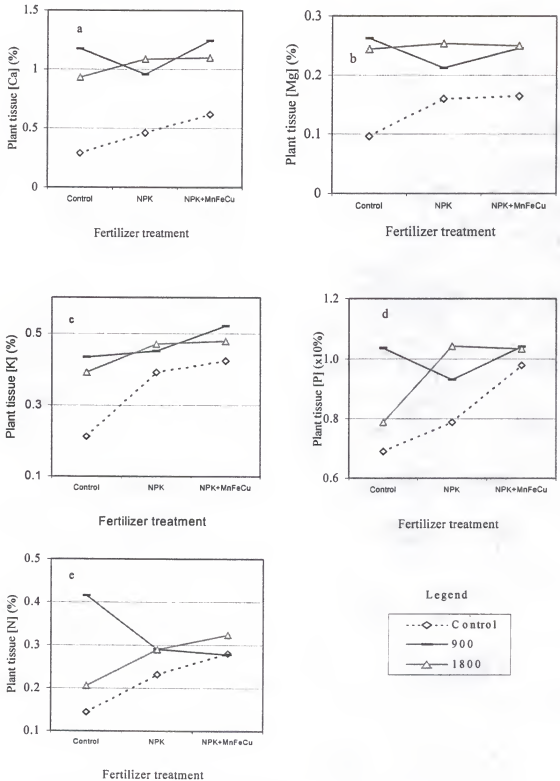


Figure 8-2. Plant tissue concentrations at the end of 10 months

Therefore increases in Ca beyond the plant requirement did not increase plant tissue Ca uptake (Table 8-1).

Similar to Ca, there was increased plant uptake of Mg from the ash-amended soil compared to the control ($p < 0.05$), due to the presence of high concentrations of Mg in the ash (Table 8-1). Ohno and Erich (1990) determined available Mg in ashes to be around 48% for Maine soils. No significant difference was observed in Mg uptake between the two ash application rates (Fig 2b) with the increase in Mg uptake being lower than that for Ca. Although ash supplied less Mg than Ca, plant requirements for Mg are also lower than for Ca, hence the close correlation between plant-available element and plant tissue concentration (Table 8-2).

The increase in K uptake compared to the control was much lower than those for Ca and Mg, not only because of lower K concentrations in ash-amended soil (Table 8-1) but also due to the greater leaching of K compared to Ca and Mg. The addition of NPK narrowed this difference (Fig. 8-2c). Ferm et al. (1992) noted significantly higher ammonium acetate-extractable K and total Ca concentrations for the topsoil in a 20 Mg ha^{-1} ash treatment than for the control. This also correlated well with plant K uptake. The high correlation between plant-available K in the soil and plant tissue concentration of K further demonstrates that K concentrations remained low. Therefore, increases in available K translated into increases in plant K uptake unlike for Ca and Mg, which were supplied well above plant requirements by the ash alone.

There was a modest increase in plant P uptake due to ash application ($p > 0.05$, Fig. 8-2d). The high correlation coefficient between plant uptake and plant-available P may be misleading, however, because it covers only a very narrow range of concentration

Table 8-2. Average soil extractable† elements from treatments used in the study, and correlations with plant tissue concentrations

	Ash treament (Mg ha^{-1})			Correlation Coefficient
	0	900	1800	
Ca	345	3420	4660	0.29
Mg	74.6	155	273	0.31
K	16.6	152	404	0.64
P	0.33	15.7	22.7	0.65
Cu	0.31	0.70	1.39	0.56
Mn	1.03	2.05	4.69	0.23
Fe	30.9	6.57	192	-0.43

†Ca, Mg, K and P were extracted using NH_4OAc, and Cu, Mn and Fe were extracted using DTPA.

change (Table 8-2). Erich (1991) observed similar patterns for corn seedlings and postulated that the P in this case was being immobilized by soil colloid surfaces and not by the modest increase in pH. In our study, pH increased by about three units and hence the nonavailability of P may have been due to precipitation of P as phosphates of Ca at high pH. Clarholm (1994) suggested that P supplements should be considered whenever wood ash is being added as a nutrient source. In addition, Clarholm's study indicated that the increase in pH would actually benefit plants grown in ash-amended soils by reducing cation leaching (through increased CEC), and by supplying basic cations (Ca, Mg and K) needed for growth.

The nitrogen content of the plants seemed to be more a function of their growth than of the treatment(s) (Fig. 8-2e). Faster-growing plants had greater dilution of N and the reverse was true for slower-growing plants (Figs. 8-1d and 8-2e). In general, plants supplied with N had better growth than those not receiving N fertilizer. Ash addition did

not affect foliar N or P concentrations for Scots pine in a study conducted by Ferm et al. (1992). However, their application rate of 20 Mg ha^{-1} was much lower than the rates used in our study.

Micronutrient Uptake

Similar to Ca, Mg, K, and P, concentrations of Fe, Mn, Cu and Zn in the ash-amended soil were much greater than in the control soil ($p < 0.05$, Table 8-1). Increased uptake of these elements, except for Fe in the ash-amended soil (Fig. 8-3), suggests that these elements were available to the plants even though the soil pH was as high as 8.6 (Table 8-1). Iron uptake was greater in the control plots than in the ash-amended pots (Fig. 8-3a). This may have been due to Fe precipitating out of solution and becoming unavailable at the high pH of the ash-amended pots. There was greater Fe uptake in the 1800 than in the 900 Mg ha^{-1} treatment ($p < 0.05$), which could be due to the greater Fe input at the higher application rate (Table 8-1). In fact, Fe was the only element to give a negative correlation coefficient (-0.43) between soil-extractable and plant tissue content.

The control did not respond to Mn addition ($p > 0.05$), while the 1800 Mg ha^{-1} treatment showed significant increase (Fig. 8-3b). The lack of response to Mn application in the control may imply that the Mn requirement of the plants had been met by native soil Mn or that too little Mn was applied in the fertilizer treatment to induce any response. We believe that the latter is true, because ash-treated plants had higher Mn uptake than the control. The 900 Mg ha^{-1} treatments showed significant reduction in Mn uptake with Mn application (Fig. 8-3b). This is in agreement with observations by Ferm et al.

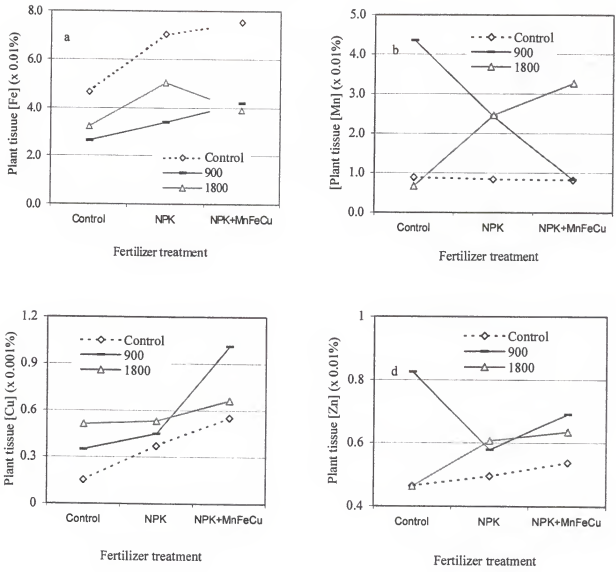


Figure 8-3. Plant tissue concentrations of micronutrients at the end of 10 months

(1992) who found that Mn uptake by Scots pine decreased with increasing ash application rate. However, the ash used in our study had a much higher Mn content (2X) and it was also applied at much higher rates. The Mn uptake for the 1800 Mg ha^{-1} treatment started off at a lower value than for the 900 Mg ha^{-1} treatment. This could be due to the high

salinity associated with the higher treatment, or to the low availability of Mn at high soil pH. Naas et al. (1993) observed that Mn was less available under conditions of high pH in coal ash-amended soils. However, when present at high concentrations, Mn is toxic to plants. The correlation coefficient between plant-available Mn and plant tissue Mn was very low in this study (0.23, Table 8-2), so it was difficult to draw concrete conclusions from only two application rates.

Greater ash application rates resulted in greater Cu uptake than for the control ($p < 0.05$, Fig 3c), suggesting that Cu in the ash was readily available to plants. Fertilization further increased Cu uptake in all three treatments. Copper had the highest correlation between plant-available Cu in soil and plant tissue concentrations of Cu among the micronutrients (r =0.56). No Zn fertilizer was added to the ash-amended soil. Nonetheless, Zn uptake from the ash-amended soil was greater than for the control, although there was no distinct trend in Zn uptake with ash application rate. A correlation coefficient of 0.01 is further testimony of this. Khanna et al. (1994) observed decreased Zn uptake by plants with papermill sludge application in rye grass and Bellamy et al. (1995) also reported lower Zn uptake with an increase papermill sludge application.

Conclusions

This study showed that, when excess wood ash is applied to slash pine, the plants grew more poorly. However, when used at more typical agronomic rates and supplemented with NPK fertilizer, ash can be beneficial as a soil amendment and supplies essential plant nutrients (Ca, Mg, K and micronutrients). High application rates should therefore be

avoided to reduce the detrimental effects posed by elevated soil pH, salinity and excessive and potentially toxic supply of micronutrients. The use of the liming equivalent of the ash in determining the application rate of ash for sustainable use to forested lands is encouraged.

CHAPTER 9
CONCLUSIONS

A few very specific conclusions can be drawn from our investigation. On the positive side, the field monitoring and greenhouse studies showed that addition of wood ash improved soil physical properties by increasing plant available water, reducing saturated hydraulic conductivity and improving the soil tilth through reduction of bulk density in our sandy soil. In addition, ash significantly increased total and available soil macronutrients (Ca, Mg, K, and P) and micronutrients (Fe, Mn, Cu, and Zn). However, when excess wood ash was applied to slash pine, the plants grew poorly.

The results from the three column studies strongly suggest that acidification of ash following application to soil is not desirable because of increased metal (Cd, Ni, Se and As) leachability. This was probably a result of calcite dissolution and subsequent release of adsorbed metals like Cd. On the other hand, the acidification of ash before application to the field greatly reduced metal solubility and leachability with the exception of Cd. Reduced metal mobility was mainly achieved through a decrease in DOC leaching upon acidification. This is of practical significance because the producers of wood ash have the option of acidifying their ashes before or during land application of ash to minimize metal leaching in soils.

The column studies on the effects of humic and fulvic acids on metal leachability showed that the extent of organic complexes transport in columns depends on their own

mobility within the system and this mobility is in itself a dynamic process governed by variable kinetics. While the soil used in this study was sandy, the addition of ash induced significant pH increases creating conditions favorable to organic matter dissolution but the high ionic strength resulting from the salts in the ash also created conditions favorable to flocculation of charged particles. In general, the prevailing soil chemical properties proved to be more important in determining the movement of metals through soil columns than the properties of the metals themselves because the soil conditions dictated the way the metals reacted with other components in the system.

In terms of application method, the subsurface application had no advantage over the surface treatment in terms of environmental impact. Apart from being cumbersome and costly, there was a shorter distance for the leachate to travel to the water table in the subsurface treatments leading to significantly higher groundwater contamination than surface application.

On the negative side, significant increases in soil pH and electric conductivity in the soil was undesirable and may adversely impact plant growth. Application of such large quantities of wood ash also adds significant amounts of other elements that have deleterious effects on plants and / or the environment in general. We strongly discourage the use of such high rates in land application of ash in forest soils. Agronomic rates based on the liming equivalent (in our case, about 40 Mg $ha^{-1,}$ to a depth of 50 cm) should be used instead. This way land application of ash can be sustainable and beneficial to forested lands.

Forest nutrient dynamics are influences by many factors. The conclusions drawn from the various studies presented in this dissertation depend on the solution

composition, pH dependent soil chemical equilibria, microbial activity and factors that affect soil hydraulic properties. Care must be taken when applying these conclusions to different situations. A full characterization of the properties of trace metals and related constituents in the particular ash and soil under the prevailing conditions of the target site must still be conducted to reduce potential harmful effects to the environment.

APPENDIX

Supplementary data from field and column studies

Groundwater samples (in the colloid study) were also acidified to different levels to determine the effects of increased DOC precipitation on elemental concentrations. However, the reduction in pH also led to dissolution of a lot of the other metal-colloidal complexes further masking the effect of pH on DOC-metal complexes.

Table A1. Concentrations of different elements (mg / kg) after treating with 0.1 and 1N HNO_3 for As and Se and concentrations of Cu, Ni and Cr after treating with 1N HNO_3.

As 0.1N HNO_3	Se 0.1N HNO_3	As 1N HNO_3	Se 1N HNO_3	Cr 1N HNO_3	Ni 1N HNO_3	Cu 1N HNO_3	pH	EC	TOC mg/L	IC mg/L	Na mg/L
1.8	0.8	0.6	1.3	29.1	26.9	15.2	8.4	1.8	118	268	569
1.7	1.9	0.8	2.1	27.1	28.5	15.1	8.1	1.1	205	129	339
2.9	8.8	1.8	9.1	35.6	23.8	16.7	7.9	1.9	438	226	659
2.9	5.2	0.9	5.8	23.5	27.7	16.5	7.8	3.7	350	464	1200
2.7	3.9	1.1	3.4	27.8	18.4	14.2	8.0	1.6	264	213	541
2.0	3.6	1.1	3.7	17.1	36.9	8.2	8.1	1.2	313	116	389
0.0	3.2	0.8	3.3	16	11.8	9.8	7.8	1.1	181	129	352
1.3	4.9	2.0	5.8	25.3	16.3	15	7.4	2.3	297	293	716
4.7	5.8	3.7	7.0	31.2	10.4	25.5	8.2	1.8	349	231	593
6.8	1.8	6.8	2.2	34.2	10.3	9.9	7.3	3.8	122	633	1270
5.2	4.8	5.3	6.1	53.4	28.5	24.1	8.2	2.2	284	298	686
2.2	1.0	11.0	6.7	84.9	29.6	45	7.5	4.3	346	697	1390
9.3	5.7	2.6	2.8	19.2	41.6	10.4	7.4	2.7	141	312	862
3.8	3.2	2.2	3.7	31.9	10.3	21.8	7.2	1.9	220	287	631

The effect of ash application on microbial biomass and activity was also determined. Below is the raw data showing how activity and biomass changed after ash application at 900 and 1800 Mg/ha.

Table A2. The release of P and TKN in the two treatment and control plots after 2 years (using the plating technique).

	Non fumigated		Fumigated	
Treatment (Mg / ha)	P	TKN	P	TKN
Control	1.2	2.1	1.4	1.8
control	0.8	2.3	1.2	2.1
control	1.5	3.8	1.1	2.1
control	1.7	2.1	2.3	1.9
control	2.1	1.9	1.9	1.5
control	1.8	1.6	1.9	1.6
900	5.0	1.7	7.9	2.1
900	5.9	1.6	8.6	2.6
900	8.3	2.3	6.7	1.8
900	6.2	1.3	7.2	1.6
900	9.6	1.8	9.5	2.1
900	9.1	1.4	5.5	1.5
1800	7.9	1.6	7.7	1.6
1800	9.3	1.5	9.7	2.0
1800	8.0	1.7	6.6	1.5
1800	6.4	1.3	6.1	1.4
1800	5.2	1.1	6.8	1.5
1800	9.2	1.3	4.9	1.2
Means				
Control	1.5	2.3	1.6	1.8
900	7.4	1.7	7.6	1.9
1800	7.7	1.4	6.9	1.5

Table A3. Bacterial and fungal populations in the two treatments and control plots after 2 years (using the plating technique).

	Batch 1	Batch 2	Mean Population (g^{-1} soil)
		Fungi	
Treatment			
control	3700	6200	4950
900	7400	1400	4400
1800	300	1300	800
		Bacteria	
control	31000000	19000000	25000000
900	5400000	5900000	5650000
1800	1300000	3300000	2300000

Various wood ash application rates were used in the experiment in Chapter 5. The same patterns observed in the high application rates (900 and 1800 Mg / ha) were observed in the lower application rates of 450 and 225 Mg / ha. The following tables show the variation of Cd, Se, Ni, Cu, Cr and As with pH and leaching period.

Table A4. The variation of Cu, Ni and Cd with pH and leaching period

Treatment	Day		
	4	7	21
Application rate / pH	Concentration mg / L		
Cu			
450/7	0	0.8	0
450/6	0.8	0.4	0
450	49	11	2.7
225/7	0.3	0.6	0
225/6	0	0.6	0
225	39	5.9	2.3
Ni			
450/7	6.3	0	16
450/6	2.3	7.8	0
450	16	1.7	0
225/7	4.7	7.5	0
225/6	5.6	0	2.1
225	33	0	24
Cd			
450/7	1.4	0.1	0
450/6	1.1	0.2	0
450	0.5	0.9	0
225/7	0.7	1.6	0
225/6	0.9	0.9	0.1
225	0.5	0.8	0

Table A5. The variation of Cu, Ni and Cd with pH and leaching period

Treatment	Day		
	4	7	21
Application rate / pH	Concentration mg / L		
Se			
450/7	5.2	1.8	1.2
450/6	4.3	2.1	1.0
450	12	3.9	1.0
225/7	3.9	1.6	1.2
225/6	3.4	1.6	0.5
225	10	3.7	0.4
As			
450/7	1.1	0.6	0.6
450/6	4.3	0.6	0.9
450	25	12	7.1
225/7	1.5	1.7	1.2
225/6	2.7	0.6	0.5
225	15	9.8	5.5
Cr			
450/7	1.8	0.1	1.5
450/6	0.2	0	0.8
450	27	3.9	7.9
225/7	0	0	1.6
225/6	0	0	1.6
225	12	0	7.5

Humic and fulvic acid and DOC extracted from the spodic horizon were used as leaching solutions in some of the column experiments from Chapters 6 and 7. Below are the concentrations of trace elements measured in the leachates.

Table A6. Concentrations of trace elements leached by humic acid extracted from the spodic horizon.

	Concentrations µg/L				
	Ni	Cr	Cu	As	Se
Pore volume					
1	140	4820	280	508	40
2	540	1790	370	76	14.1
3	549	409	291	47.9	1.3
4	29	107	37	13.2	0
5	38	67	39	2.6	0
6	181	560	53	2.8	0
7	297	658	85	0	0
8	42	64	44	0	0
9	82	89	42	0	0
10	59	18	40	0.1	0

Table A7. Concentrations of trace elements leached by fulvic acid extracted from the spodic horizon.

	Concentrations µg/L				
	Ni	Cr	Cu	As	Se
Pore volume					
1	220	4100	300	460	68
2	560	1350	390	65.2	15.1
3	35	296	62	33.2	0
4	29	105	50	14	0
5	23	68	38	1.3	0
6	45	61	43	0	0
7	72	53	40	0	0
8	422	110	284	0	0
9	73	90	40	0	0
10	57	197	38	0	0

Table A8. Concentrations of trace elements leached by DOC extracted from the spodic horizon.

	Concentrations µg/L				
	Ni	Cr	Cu	As	Se
Pore volume					
1	1530	5670	360	378	14
2	450	1960	390	95.8	57.4
3	454	628	448	32.3	0
4	20	164	54	0	0
5	25	81	43	2.4	0
6	13	9.5	6	2.7	0
7	37	126	39	0	0
8	66	161	45	0	0
9	45	182	41	13.8	0
10	270	302	419	6.1	0

Table A9. Total amounts of Cu, Ni , inorganic carbon and DOC leached in the first 50 mL and ionic strength and pH in first pore volume of each column

Leaching solution	Column material	Copper	Nickel	DOC	In C	I (mol dm^{-3})	Initial pH†
		------- µg ------		----- mg ----			
Deionized water	Ash	360 a	50 a	48	580	0.20	10
Deionized water	Ash + A	320 b	79 a	210	660	0.23	10
Deionized water	Ash + A + Bh	320 b	73 b	390	1280	0.21	10
HA	Ash	66 c	35 b	4	450	0.38	11
FA	Ash	11 d	7 c	1	490	0.36	11
HAFA	Ash	64 c	44 a	14	850	0.39	11

* Means within a column followed by the same letter are not significantly different ($p<0.05$) using Student t-test.

† pH values initially started off high in both sets of columns but they decreased to ~ 9.5 after 50 mL leachate had eluted through the columns

Table A10. Concentrations of other elements from columns packed with soil from different horizons (leached by water).

	Concentration µg/L					
Column material – Pore volume	Ca	P	Zn	Al	Fe	Ni
M1-2	2	21	0	14	0.1	0
M1-3	2	3	0.3	19	1.8	8.4
M1-4	2	1	0.2	30	2.6	7.6
M1-5	1	0	0.1	24	1.8	3.5
M1-6	1	1	0	20	1.2	1.9
M2-2	21	27	0.4	20	6.1	1.7
M2-3	32	15	0.1	222	4.6	0.3
M2-4	24	9	0.2	111	3.7	1.7
M2-5	10	4	0.1	64	1.5	0.6
M2-6	5	3	0.1	34	0.3	0
M3-2	17	54	0	24	2.8	0.2
M3-3	29	46	0.2	410	5.8	0
M3-4	21	31	0.1	473	3.8	0
M3-5	7	11	0	249	1.3	0
M3-6	4	6	0.1	93	1.8	0.9

Table A11. Concentrations of other elements leached from ash packed columns by DOC extracted from the spodic horizon.

	Concentration µg/L					
Leaching solution – Pore volume	Ca	P	Zn	Al	Fe	Ni
FA-3	2	24	0.4	108	0.8	1.4
FA-4	4	6	0.4	2	0.8	1.4
FA-5	0	0	0	0	0	0
FA-6	2	4	0	0	0	0
HA-3	4	16	0	0	4.4	5.2
HA-4	2	14	0	0	0	0.2
HA-5	0	8	0	18	0.4	1.6
HA-6	2	4	0	30	0.2	0.4
HAFA-3	2	40	0	2	0	0
HAFA-4	4	10	0.2	2	0.6	2.6
HAFA-5	2	4	0	0	0	0
HAFA-6	4	2	0.4	6	2	1.2
HAFAB-1	8	300	0	4	0.2	0
HAFAB-3	2	34	0.4	2	2.4	0.4
HAFAB-5	0	2	0	6	0	0

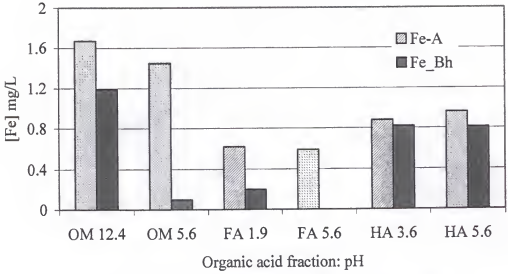


Figure A1. Fe variation with pH in the different leachates

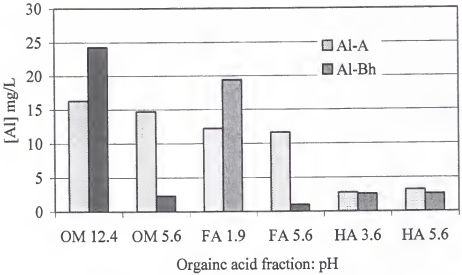


Figure A2. Variation with pH in the different leachates

OM : organic matter (dissolved)
FA: fulvic acid and HA: humic acid

Table A12. Measured pH, EC and organic matter in soil from the field plots

Treatment	pH				EC(ms cm^{-1})			OM (%)				
Depth (cm)	1/29/96	4/29/96	7/25/96	11/12/96	1/29/96	4/29/96	7/25/96	11/12/96	1/29/96	4/29/96	7/25/96	11/12/96
900 subsurface												
0-20	9.59±0.03	9.37±0.12	8.71±0.21	8.33±0.13	0.91±0.15	0.30±0.02	0.16±0.05	0.15±0.00	0.40±0.10	0.27±0.15	0.23±0.06	0.27±0.06
20-40	9.78±0.08	9.54±0.03	9.00±0.11	8.68±0.15	1.76±0.47	0.41±0.03	0.25±0.10	0.22±0.03	0.33±0.23	0.17±0.15	0.27±0.06	0.13±0.12
40-60	9.93±0.12	9.72±0.13	9.22±0.10	8.68±0.42	3.47±1.06	0.58±0.05	0.34±0.11	0.26±0.05	0.23±0.06	0.20±0.10	0.10±0.06	0.07±0.12
60-80	9.84±0.03	9.59±0.28	9.19±0.18	8.58±0.06	2.98±0.58	0.40±0.07	0.36±0.10	0.15±0.06	0.37±0.21	0.10±0.10	0.03±0.00	0.23±0.06
80-100	9.62±0.05	9.57±0.16	9.18±0.26	8.78±0.13	2.00±0.56	0.33±0.07	0.35±0.14	0.17±0.01	0.17±0.06	0.00±0.00	0.23±0.06	0.13±0.15
Bh	7.23±0.54	8.92±0.34	---- *	8.88±0.10	0.59±0.94	0.35±0.02	----	0.18±0.05	0.17±0.06	0.20±0.17	----	0.17±0.21
1800 subsurface												
0-20	9.69±0.08	9.69±0.05	8.57±0.41	8.75±0.28	1.20±0.28	0.53±0.13	0.25±0.05	0.24±0.03	0.60±0.10	0.53±0.12	0.43±0.31	0.63±0.15
20-40	9.98±0.09	9.74±0.07	8.95±0.29	8.95±0.19	2.76±0.77	0.62±0.07	0.42±0.05	0.39±0.07	0.53±0.12	0.40±0.00	0.37±0.06	0.63±0.21
40-60	10.09±0.07	9.95±0.18	9.34±0.09	9.06±0.19	5.31±1.00	0.84±0.12	0.47±0.10	0.39±0.10	0.50±0.20	0.30±0.10	0.40±0.17	0.17±0.12
60-80	9.90±0.10	9.83±0.22	9.33±0.13	8.86±0.02	3.87±1.29	0.89±0.34	0.51±0.08	0.29±0.03	0.37±0.12	0.27±0.15	0.10±0.00	0.10±0.00
80-100	9.73±0.02	9.75±0.14	9.21±0.06	8.89±0.20	2.66±0.50	0.61±0.14	0.36±0.10	0.28±0.05	0.13±0.06	0.07±0.06	0.13±0.06	0.17±0.15
Bh	7.95±1.08	9.54±0.10	----	8.91±0.34	0.42±0.40	0.64±0.37	----	0.30±0.03	0.17±0.12	0.17±0.12	----	0.30±0.36
900 surface												
0-20	9.77±0.27	9.16±0.21	8.37±0.17	8.07±0.14	5.25±3.75	0.41±0.14	0.20±0.04	0.17±0.02	0.90±0.40	0.87±0.31	0.90±0.36	0.93±0.25
20-40	9.66±0.41	9.37±0.09	8.71±0.17	8.56±0.08	4.20±4.57	0.59±0.04	0.33±0.05	0.28±0.05	0.83±0.21	0.80±0.35	0.87±0.15	0.83±0.35
40-60	9.52±0.21	9.70±0.13	9.08±0.12	8.72±0.09	1.99±0.49	0.69±0.14	0.50±0.07	0.27±0.04	0.67±0.31	0.47±0.55	0.63±0.15	0.60±0.20
60-80	9.34±0.25	9.44±0.10	9.07±0.19	8.66±0.09	1.40±0.42	0.42±0.11	0.33±0.05	0.23±0.07	0.40±0.17	0.30±0.00	0.50±0.26	0.37±0.21
80-100	8.83±0.76	9.43±0.24	9.07±0.13	8.59±0.14	0.77±0.67	0.38±0.06	0.35±0.06	0.20±0.08	0.33±0.21	0.17±0.06	0.20±0.10	0.30±0.17
Bh	7.27±0.12	7.81±0.72	----	8.62±0.45	0.06±0.01	0.22±0.02	----	0.27±0.09	0.40±0.30	0.17±0.06	----	0.30±0.10
1800 surface												
0-20	9.96±0.22	9.60±0.07	8.72±0.14	8.38±0.18	6.44±4.38	0.56±0.06	0.37±0.03	0.28±0.06	1.20±0.46	0.90±0.26	1.13±0.35	1.03±0.45
20-40	10.08±0.11	9.78±0.04	9.18±0.12	8.51±0.20	7.16±3.26	0.74±0.15	0.63±0.06	1.39±1.91	1.07±0.25	0.93±0.25	1.00±0.17	0.93±0.21
40-60	10.01±0.07	9.89±0.22	9.36±0.14	8.74±0.11	5.44±1.20	1.08±0.53	0.81±0.14	1.49±1.93	1.07±0.25	0.53±0.40	0.57±0.06	0.67±0.38
60-80	9.78±0.05	9.88±0.18	9.31±0.01	8.83±0.08	2.92±0.22	1.11±0.42	0.69±0.04	1.26±1.54	0.20±0.10	0.33±0.12	0.33±0.12	0.40±0.20
80-100	8.94±0.61	9.86±0.04	9.24±0.01	8.79±0.19	0.97±1.10	0.99±0.23	0.58±0.06	1.29±1.64	0.20±0.10	0.37±0.31	0.23±0.12	0.37±0.21
Bh	8.11±1.05	8.48±1.07	----	9.19±0.21	0.33±0.39	0.56±0.33	----	1.83±2.48	0.23±0.15	0.20±0.17	----	0.20±0.00
Control												
0-20	5.19±0.13	5.43±0.21	5.50±0.10	5.38±0.15	0.02±0.00	0.05±0.03	0.02±0.00	0.02±0.00	0.87±0.12	0.63±0.21	0.57±0.06	0.77±0.06
20-40	5.43±0.11	5.49±0.14	5.57±0.11	5.44±0.24	0.02±0.00	0.03±0.01	0.02±0.00	0.02±0.00	0.33±0.12	0.33±0.06	0.37±0.12	0.50±0.17
40-60	5.21±0.38	5.69±0.17	5.44±0.25	5.48±0.28	0.02±0.00	0.03±0.01	0.02±0.00	0.03±0.02	0.30±0.10	0.27±0.12	0.23±0.06	0.37±0.15
60-80	5.33±0.24	5.52±0.37	5.44±0.12	5.42±0.24	0.02±0.00	0.10±0.10	0.03±0.00	0.02±0.00	0.23±0.06	0.23±0.06	0.13±0.06	0.23±0.21
80-100	5.28±0.17	5.46±0.06	5.63±0.12	5.47±0.31	0.02±0.00	0.06±0.05	0.03±0.00	0.02±0.00	0.17±0.06	0.13±0.06	0.13±0.06	0.33±0.12
Bh	5.32±0.12	5.49±0.15	----	5.52±0.45	0.02±0.00	0.03±0.01	----	0.02±0.00	0.10±0.10	0.23±0.12	----	0.23±0.06

* Soil at Bh horizon was too wet to collect

Table A13. Measured As, Cr, and Se concentrations in soil

Treatment	As (mg kg^{-1})				Cr (mg kg^{-1})				Fe (mg kg^{-1})			
Depth (cm)	1/29/96	4/29/96	7/25/96	11/1296	1/29/96	4/29/96	7/25/96	11/12/96	1/29/96	4/29/96	7/25/96	11/12/96
900 subsurface												
0-20	1.00±0.85	0.89±0.60	0.73±0.55	0.60±0.53	1.15±1.03	4.86±0.68	2.13±2.00	0.80±1.13	1.14±0.11	1.32±0.22	1.11±0.25	0.99±0.46
20-40	1.85±0.37	1.65±0.19	1.13±0.29	0.90±0.17	1.58±0.48	4.37±0.51	1.77±0.29	0.60±0.17	1.10±0.16	1.19±0.25	0.95±0.16	0.97±0.29
40-60	0.67±0.32	1.54±1.08	0.60±0.20	0.73±0.32	1.68±0.56	4.24±0.80	0.90±0.35	0.67±0.40	1.03±0.23	1.09±0.17	0.94±0.09	1.02±0.17
60-80	1.64±0.56	1.13±0.20	0.70±0.26	0.50±0.17	1.09±1.02	3.43±0.66	1.07±0.83	0.67±0.38	1.13±0.08	0.82±0.33	0.70±0.21	0.89±0.04
80-100	0.46±0.19	0.80±0.38	0.63±0.21	0.53±0.32	1.15±1.12	3.20±0.51	1.27±0.38	0.33±0.25	0.76±0.29	0.71±0.26	0.52±0.30	0.48±0.20
Bh	1.53±0.37	0.93±0.80	----	0.67±0.70	1.03±0.94	5.23±0.92	----	1.10±0.40	0.27±0.06	0.71±0.84	----	0.18±0.05
1800 subsurface												
0-20	1.32±0.32	1.30±0.57	0.77±0.15	0.57±0.74	2.67±1.10	5.83±0.55	1.30±0.87	1.00±0.46	1.69±0.08	1.64±0.26	1.11±0.27	1.83±0.46
20-40	1.32±0.32	1.00±0.93	0.97±0.29	0.22±0.38	2.26±0.71	5.28±0.61	0.73±0.57	0.40±0.00	1.44±0.04	1.50±0.25	1.01±0.19	1.46±0.19
40-60	1.10±0.81	1.15±0.11	0.57±0.15	0.17±0.29	2.28±0.77	5.19±0.37	0.50±0.10	0.50±0.26	1.39±0.07	1.45±0.25	1.10±0.20	1.20±0.54
60-80	1.43±0.37	0.74±0.53	0.47±0.57	0.17±0.29	2.91±1.63	4.19±0.80	0.83±0.06	1.00±0.35	0.97±0.12	0.67±0.52	0.80±0.25	0.70±0.22
80-100	1.00±0.64	0.95±0.33	0.80±0.46	0.23±0.40	1.46±1.42	3.90±0.37	0.93±0.29	0.83±0.55	0.72±0.04	0.82±0.19	0.62±0.35	0.47±0.35
Bh	0.88±0.76	0.26±0.04	----	0.13±0.23	1.48±1.50	3.38±0.87	----	0.60±0.50	0.18±0.10	0.67±0.64	----	0.23±0.17
900 surface												
0-20	0.31±0.53	1.00±0.72	0.33±0.31	0.27±0.38	3.95±0.37	4.14±0.61	1.23±0.15	0.87±0.50	1.17±0.33	1.21±0.23	1.08±0.29	1.27±0.17
20-40	0.86±1.05	0.84±0.14	0.40±0.10	0.30±0.10	3.69±0.84	4.39±0.87	0.57±0.40	0.53±0.12	1.09±0.16	1.20±0.23	0.98±0.17	1.23±0.21
40-60	0.74±0.67	0.69±0.26	0.50±0.20	0.20±0.00	3.64±0.72	3.60±0.31	0.75±0.56	0.77±0.31	1.00±0.23	1.08±0.03	0.95±0.23	1.01±0.19
60-80	0.00±0.00	0.36±0.23	0.20±0.17	0.20±0.17	3.01±0.76	3.34±0.63	0.67±0.40	0.60±0.17	0.78±0.15	0.81±0.18	0.43±0.40	0.82±0.30
80-100	0.00±0.00	1.06±0.27	0.47±0.40	0.30±0.10	2.99±0.38	3.40±0.44	0.93±0.47	0.50±0.30	0.79±0.18	0.79±0.15	0.71±0.14	0.81±0.27
Bh	0.00±0.00	0.43±0.24	----	0.07±0.06	2.81±1.31	3.21±1.00	----	0.63±0.40	0.17±0.14	0.19±0.15	----	0.21±0.16
1800 surface												
0-20	0.86±0.75	1.11±0.27	0.53±0.23	0.27±0.12	5.43±0.78	5.98±3.84	1.87±0.68	1.43±0.65	1.86±0.27	1.69±0.26	1.60±0.23	1.48±0.22
20-40	0.49±0.47	1.26±0.43	0.13±0.12	0.23±0.21	4.95±1.21	5.64±0.44	2.03±0.64	1.50±0.35	1.56±0.45	1.74±0.29	1.50±0.29	1.60±0.31
40-60	0.74±1.12	0.89±0.30	0.20±0.17	0.37±0.23	4.51±1.19	4.70±1.69	1.70±0.53	0.97±0.51	1.43±0.37	1.20±0.50	1.18±0.15	1.08±0.32
60-80	0.31±0.53	0.45±0.20	0.20±0.10	0.20±0.10	3.33±0.85	3.44±0.59	1.13±0.49	1.23±0.67	0.82±0.06	0.89±0.24	0.79±0.05	0.86±0.25
80-100	0.00±0.00	0.93±0.23	0.37±0.15	0.20±0.17	3.10±0.59	3.98±0.80	1.30±0.10	0.93±0.06	0.82±0.16	1.01±0.34	0.70±0.09	0.78±0.22
Bh	0.00±0.00	0.23±0.00	----	0.23±0.21	2.99±0.57	3.60±0.76	----	0.70±0.17	0.17±0.10	0.12±0.01	----	0.36±0.30
Control												
0-20	0.31±0.53	0.43±0.07	0.20±0.17	0.33±0.06	2.05±1.78	3.92±1.62	1.33±0.57	1.07±0.45	0.66±0.10	0.98±0.35	0.74±0.08	0.51±0.34
20-40	0.18±0.32	0.36±0.23	0.30±0.00	0.23±0.15	2.02±1.76	3.36±0.15	0.87±0.25	0.67±0.25	0.72±0.06	0.78±0.02	0.70±0.04	0.72±0.10
40-60	0.18±0.32	0.45±0.38	0.37±0.12	0.23±0.15	2.05±1.80	3.18±0.23	0.77±0.23	0.80±0.10	0.71±0.08	0.77±0.07	0.74±0.01	0.74±0.06
60-80	0.00±0.00	0.47±0.26	0.20±0.17	0.23±0.06	2.92±0.69	3.11±0.34	0.47±0.31	0.50±0.10	0.71±0.08	0.73±0.11	0.71±0.14	0.71±0.08
80-100	0.31±0.53	0.30±0.11	0.27±0.12	0.20±0.20	1.89±1.76	3.07±0.37	0.67±0.06	0.57±0.15	0.46±0.40	0.75±0.11	0.69±0.12	0.71±0.08
Bh	0.00±0.00	0.23±0.00	----	0.23±0.21	2.34±2.04	3.12±0.312	----	0.67±0.21	0.10±0.08	0.14±0.05	----	0.16±0.06

Table A14. Measured Ca, Mg and K concentrations in soil

Treatment	Ca (g kg^{-1})				Mg (g kg^{-1})				K (g kg^{-1})			
Depth (cm)	1/29/96	4/29/96	7/25/96	11/12/96	1/29/96	4/29/96	7/25/96	11/12/96	1/29/96	4/29/96	7/25/96	11/12/96
900 subsurface												
0-20	8.50±0.12	6.05±1.39	5.04±1.39	6.14±3.73	0.67±0.06	0.66±0.12	0.56±0.14	0.61±0.35	0.39±0.10	0.31±0.08	0.25±0.05	0.21±0.16
20-40	5.79±2.66	4.55±1.46	3.86±1.26	3.12±2.14	0.48±0.11	0.51±0.11	0.45±0.13	0.39±0.22	0.38±0.09	0.30±0.05	0.24±0.07	0.18±0.09
40-60	4.01±1.07	4.21±0.82	3.89±0.89	3.21±2.02	0.41±0.05	0.49±0.04	0.45±0.06	0.40±0.19	0.39±0.06	0.29±0.05	0.26±0.02	0.20±0.05
60-80	3.61±1.44	1.04±0.83	0.94±0.22	2.45±2.55	0.35±0.07	0.17±0.09	0.16±0.02	0.30±0.25	0.38±0.11	0.15±0.06	0.16±0.02	0.17±0.09
80-100	0.82±0.40	0.26±0.11	0.18±0.06	0.54±0.49	0.05±0.01	0.09±0.01	0.05±0.02	0.09±0.07	0.13±0.06	0.09±0.01	0.08±0.03	0.08±0.02
Bh	0.49±0.13	4.81±0.08	----	0.31±0.18	0.02±0.00	0.46±0.74	----	0.04±0.02	0.01±0.01	0.27±0.31	----	0.05±0.03
1800 subsurface												
0-20	14.51±4.28	12.06±1.52	8.51±3.02	13.65±4.57	1.39±0.37	1.23±0.16	0.85±0.26	1.37±0.36	0.73±0.16	0.58±0.07	0.33±0.10	0.52±0.12
20-40	10.83±3.90	10.09±1.83	6.49±2.80	9.97±0.84	1.05±0.32	1.03±0.13	0.69±0.27	1.05±0.05	0.67±0.16	0.53±0.08	0.31±0.08	0.48±0.02
40-60	9.99±2.02	9.77±3.12	7.15±1.17	6.52±6.99	0.97±0.18	1.00±0.25	0.79±0.16	0.69±0.62	0.78±0.09	0.55±0.11	0.41±0.10	0.36±0.25
60-80	4.93±3.20	3.23±4.16	1.89±0.25	1.01±0.68	0.47±0.23	0.35±0.40	0.26±0.06	0.16±0.07	0.52±0.15	0.24±0.20	0.21±0.06	0.13±0.01
80-100	1.19±0.75	1.92±1.70	0.59±0.58	0.55±0.55	0.13±0.07	0.25±0.15	0.11±0.11	0.08±0.07	0.29±0.05	0.23±0.08	0.15±0.08	0.11±0.02
Bh	0.35±0.07	2.43±3.58	----	0.56±0.47	0.02±0.02	0.29±0.39	----	0.07±0.05	0.01±0.02	0.27±0.20	----	0.11±0.05
900 surface												
0-20	6.70±3.01	6.79±1.85	5.09±2.93	6.66±1.41	0.73±0.34	0.77±0.25	0.62±0.32	0.75±0.14	0.66±0.41	0.41±0.14	0.29±0.14	0.32±0.04
20-40	5.69±2.02	5.17±0.59	3.55±1.07	6.59±2.36	0.55±0.11	0.60±0.09	0.45±0.11	0.74±0.24	0.50±0.16	0.37±0.10	0.26±0.10	0.40±0.11
40-60	3.87±0.81	6.17±2.44	3.55±1.93	3.75±3.43	0.44±0.11	0.59±0.12	0.44±0.21	0.45±0.35	0.47±0.15	0.41±0.08	0.28±0.11	0.27±0.12
60-80	0.92±0.70	0.53±0.34	0.18±0.15	2.15±3.04	0.14±0.09	0.13±0.03	0.06±0.06	0.29±0.32	0.17±0.16	0.15±0.05	0.10±0.08	0.21±0.12
80-100	0.57±0.26	0.23±0.05	0.39±0.16	1.92±2.87	0.11±0.06	0.11±0.02	0.12±0.05	0.27±0.31	0.10±0.03	0.14±0.03	0.15±0.02	0.19±0.10
Bh	0.98±1.34	0.09±0.02	----	0.47±0.37	0.02±0.02	0.02±0.00	----	0.05±0.04	0.01±0.01	0.01±0.02	----	0.07±0.06
1800 surface												
0-20	15.57±4.50	12.93±1.25	12.69±2.13	10.28±2.02	1.54±0.40	1.39±0.15	1.40±0.19	1.15±0.24	1.57±0.80	0.72±0.14	0.57±0.09	0.45±0.07
20-40	12.87±5.28	13.49±2.42	12.10±4.06	10.60±0.90	1.27±0.48	1.43±0.23	1.36±0.42	1.17±0.09	1.29±0.54	0.76±0.13	3.53±5.17	0.53±0.01
40-60	11.08±6.27	6.67±5.26	7.91±2.28	5.21±3.88	1.09±0.48	0.77±0.56	0.91±0.22	0.64±0.42	1.17±0.50	0.56±0.31	0.51±0.11	0.38±0.17
60-80	2.37±0.60	1.75±1.15	1.63±1.19	1.87±1.98	0.29±0.06	0.27±0.14	0.26±0.11	0.26±0.23	0.40±0.09	0.30±0.11	0.26±0.02	0.23±0.10
80-100	1.19±0.33	3.75±5.45	0.54±0.28	1.07±1.38	0.14±0.02	0.45±0.54	0.13±0.01	0.19±0.17	0.19±0.10	0.42±0.30	0.18±0.02	0.19±0.09
Bh	0.80±0.46	0.21±0.12	----	0.45±0.33	0.07±0.06	0.03±0.01	----	0.07±0.01	0.07±0.12	0.05±0.05	----	0.11±0.06
Control												
0-20	1.27±1.74	0.09±0.02	0.09±0.03	0.27±0.32	0.09±0.03	0.09±0.01	0.09±0.01	0.07±0.01	0.03±0.03	0.03±0.01	0.07±0.03	0.05±0.04
20-40	0.18±0.13	0.05±0.01	0.09±0.02	0.07±0.02	0.07±0.01	0.09±0.01	0.09±0.01	0.07±0.01	0.01±0.01	0.02±0.02	0.06±0.02	0.03±0.01
40-60	0.56±0.69	0.07±0.01	0.07±0.01	0.07±0.01	0.07±0.01	0.09±0.01	0.09±0.01	0.08±0.02	0.02±0.00	0.01±0.01	0.11±0.10	0.02±0.02
60-80	1.29±1.62	0.05±0.01	0.12±0.07	0.05±0.01	0.08±0.02	0.09±0.01	0.11±0.06	0.08±0.00	0.03±0.01	0.03±0.01	0.06±0.00	0.03±0.01
80-100	0.08±0.12	0.05±0.01	0.35±0.51	0.07±0.03	0.04±0.03	0.09±0.02	0.11±0.06	0.08±0.00	0.01±0.01	0.03±0.01	0.05±0.02	0.04±0.00
Bh	0.13±0.10	0.03±0.01	----	0.04±0.00	0.01±0.01	0.01±0.01	----	0.01±0.01	0.00±0.00	0.00±0.00	----	0.01±0.01

Table A15. Measured P and Al in the soil

Treatment	P (g kg^{-1})				Al (g kg^{-1})			
Depth (cm)	1/29/96	4/29/96	7/25/96	11/12/96	1/29/96	4/29/96	7/25/96	11/12/96
900 subsurface								
0-20	0.28±0.02	0.24±0.03	0.23±0.06	0.24±0.12	2.01±0.14	2.50±0.31	3.18±1.33	1.59±0.60
20-40	0.23±0.04	0.21±0.01	0.21±0.06	0.18±0.05	2.21±0.38	2.45±0.40	2.32±0.38	2.00±0.37
40-60	0.22±0.02	0.21±0.02	0.21±0.01	0.18±0.02	1.96±0.58	2.38±0.35	2.15±0.32	2.14±0.18
60-80	0.21±0.03	0.14±0.02	0.13±0.02	0.16±0.05	2.20±0.53	1.96±0.50	2.14±1.23	1.85±0.32
80-100	0.10±0.00	0.10±0.02	0.08±0.06	0.09±0.02	1.15±0.27	1.66±0.43	1.69±0.85	1.28±0.11
Bh	0.05±0.02	0.20±0.26	----	0.06±0.02	0.77±0.29	1.89±1.06	----	0.92±0.29
1800 subsurface								
0-20	0.50±0.11	0.43±0.06	0.28±0.07	0.44±0.09	2.85±0.39	3.01±0.67	2.49±1.23	2.90±0.44
20-40	0.45±0.09	0.37±0.03	0.25±0.08	0.38±0.02	2.40±0.15	2.89±0.62	3.37±2.86	2.72±0.85
40-60	0.43±0.03	0.37±0.06	0.29±0.06	0.28±0.16	2.43±0.23	2.76±0.54	2.45±0.72	2.43±0.68
60-80	0.29±0.08	0.18±0.14	0.18±0.05	0.15±0.03	1.94±0.31	1.37±0.66	2.89±0.52	1.82±0.55
80-100	0.15±0.03	0.19±0.02	0.15±0.05	0.11±0.02	1.53±0.09	2.13±0.55	3.45±3.70	1.41±0.18
Bh	0.07±0.02	0.17±0.13	----	0.09±0.02	0.99±0.37	1.98±1.02	----	1.15±0.27
900 surface								
0-20	0.41±0.17	0.37±0.09	0.31±0.10	0.35±0.06	2.37±0.74	2.67±0.84	4.20±1.35	2.48±0.54
20-40	0.35±0.05	0.31±0.05	0.27±0.06	0.35±0.08	2.35±0.78	2.54±0.74	6.95±7.99	2.48±0.70
40-60	0.31±0.08	0.31±0.08	0.26±0.10	0.25±0.12	2.11±0.82	2.15±0.46	3.66±1.39	2.23±0.68
60-80	0.14±0.05	0.13±0.03	0.09±0.06	0.19±0.13	1.84±0.71	2.17±0.76	1.12±1.20	2.06±0.90
80-100	0.13±0.03	0.09±0.02	0.11±0.01	0.17±0.12	1.99±0.90	2.24±0.63	2.17±0.81	2.08±0.76
Bh	0.07±0.04	0.05±0.01	----	0.07±0.04	1.11±0.66	0.91±0.54	----	0.96±0.60
1800 surface								
0-20	0.68±0.20	0.55±0.09	0.52±0.04	0.45±0.10	2.89±0.46	2.89±0.56	4.54±2.18	2.46±0.62
20-40	0.59±0.21	0.56±0.08	0.52±0.11	0.47±0.05	2.61±0.55	3.02±0.63	3.20±0.10	2.62±0.59
40-60	0.53±0.20	0.35±0.19	0.40±0.06	0.33±0.15	2.56±0.57	2.30±.083	3.21±1.47	2.31±0.87
60-80	0.21±0.03	0.19±0.04	0.21±0.02	0.22±0.09	1.71±0.06	1.99±.074	3.45±2.45	2.05±0.77
80-100	0.14±0.02	0.23±0.20	0.15±0.02	0.17±0.06	1.97±0.61	2.23±0.33	5.43±3.93	2.01±0.72
Bh	0.09±0.04	0.07±0.01	----	0.09±0.03	0.95±0.54	0.93±0.71	----	1.11±0.74
Control								
0-20	0.11±0.02	0.10±0.02	0.13±0.03	0.10±0.04	1.65±0.32	2.07±0.13	4.80±2.78	1.27±0.69
20-40	0.12±0.02	0.10±0.02	0.11±0.01	0.12±0.02	1.88±0.12	2.28±0.17	4.28±2.05	1.88±0.35
40-60	0.11±0.01	0.10±0.02	0.11±0.01	0.11±0.01	1.80±0.14	2.19±0.07	5.06±1.72	1.97±0.23
60-80	0.12±0.04	0.07±0.01	0.11±0.03	0.09±0.01	1.82±0.09	2.01±0.13	3.45±2.38	1.81±0.11
80-100	0.06±0.05	0.07±0.01	0.09±0.02	0.09±0.01	1.13±0.99	1.98±0.17	1.90±0.23	1.79±0.09
Bh	0.05±0.01	0.05±0.01	----	0.05±0.01	0.79±0.32	0.71±0.08	----	0.69±0.11

Not determined

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BIOGRAPHICAL SKETCH

Tait Chirenje was born in Zimbabwe on 11 August, 1971, and did his elementary and high school education in Harare and Mutare respectively. He enrolled at the University of Zimbabwe in 1991 and completed his Bachelor of Science degree in soil science graduating with honors in December 1993. Tait enrolled for a Master of Science degree in environmental earth science at the University of Guelph, Ontario, Canada, in January 1994 and graduated in June 1996.

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I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

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I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

Willie G. Harris
Professor of Soil and Water Science

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Ramon C. Littell
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